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Annual INREP Report for 2021

Submitted to the Israeli High Committee of High Education (CHE) and to the international board of INREP, by INREP steering committee:

Emauel Peled (TAU), Yair Ein-Eli (Technion), Lior Elbaz (BIU), Diana Golodnitsky (TAU), Yoed Tsur (Technion), Shalom Luski, administrative manager, BIU), Doron Aurbach (head, BIU)

1. **Vision.**

In the field of **batteries,** we continue to bring Li ion batteries to their true horizon in terms of energy density, stability, safety and long cycle life. We identified the best directions re: cathodes, anodes and electrolyte solutions.

We can emphasize a continues, fully justified work by 4 groups at BIU & TAU on novel, high specific capacity Si anodes. We came this year with new ideas that are being applied during recent months. We identified also the most energetic cathode materials that can ensure also excellent cycle life and reasonable safety features.

We are already working intensively in the challenging field of solid-state batteries based on active metal anodes. The relevant anodes are lithium or sodium metal foils. The use of solid electrolytes enables their use in rechargeable, high energy density batteries. We developed new solid electrolyte concepts.

We are demonstrating highly energetic Li-sulfur batteries.

We continue to explore fundamental aspects related to rechargeable Mg batteries, concentrated this year on a new electrolyte system and polymeric cathodes.

We concluded our fundamental studies related to Li-oxygen batteries.

We are also working on battery systems for large energy storage, because this issue is going to be a major challenge in our energy economy. We made an impressive progress in developing rechargeable aqueous sodium batteries. We started developing rechargeable zinc batteries.

We are interested in entering the field of power sources for microelectronics and wearables, and in the development of novel approaches and technologies for the fabrication of thin-film, free form-factor printed batteries. A comprehensive work in these directions is pursued at TAU.

In the field of **Fuel Cells, t**he main theme is still to reduce cost and increase durability of PEMFCs and AEMFCs.

There are side important projects related to developing new analytical techniques. These include EQCM based techniques, on-line mass spectrometry, solid-state NMR and terahertz spectroscopy.

We established relationship with dozens of energy scientists from Morocco, through our distinguished international board member , Dr. Khalil Amine, an American citizen , senior scientist in Argonne National Laboratory, USA, who is also a Moroccan citizen, intensively connected to the scientific community in

Morocco. We set an extensive collaboration program between INREP PIs and Moroccan partners from several universities their. The Moroccan side as a promised support of 20 million USD for 5 years for this collaboration, through OTP, the big chemical company in Morocco. We are organizing in these days the financial aspects of this collaboration at this end. We are in contact with the Chief Scientists in the Ministries of Energy, Science and Technology of Israel (Dr. Gideon Friedman and Prof. Avi Domb). We hope to conclude all these efforts in the next months, starting formal bi-national collaboration already in 2022. We believe that such collaboration may be considered as a geopolitical breakthrough in the middle east.

2. **Next year - 2022**

The academic year October 2019 - September 2020 was the 10^{th} and last formal year of INREP - supported by the Israeli CHE & Prime Minister Office. We continue with INREP during 2021 and 2022 through the use of internal resources and thanks to excellent networking & collaboration h

We extended the work within INREP to also address the great challenge of large energy storage. We show that INREP has a capability to meet other energy challenges, beyond electro-mobility. The most important one is indeed development of reliable electrochemical technologies for large energy storage. Here key importance is cost, very prolonged durability, low hysteresis (i.e. reaching high energy efficiency per cycle) and the use of most abundant and available elements.

In this branch of efforts, work on super-capacitors is being merged. We are demonstrating hybrid systems in which the negative electrode is carbonaceous with surface red-ox activity, while the cathodes are comprising Li and Na intercalation compounds. The most important cathode materials are lithiated and sodiated manganese oxide compounds.

During 2021 we started to develop systematically Na ion battery systems for large energy storage.

The anodes should be carbonaceous (hard carbons that we develop), the cathodes are based on sodiated manganese oxide compounds containing other metallic elements like Ti, Fe, Li, Ni (the latter two in small amount at a doping level).

The electrolyte solutions are based on propylene carbonate (PC) and $NaPF_6$ + additives & co-solvents. The use of PC as a main solvent ensures safety, cost-effectiveness and large enough electrochemical window.

In our work on fuel cell, we continue focusing on advanced materials for PEMFCs while increasing our effort in the development of AEMFCs in support of the Israeli industry in this field. We combine the best developed materials to show high performance in fuel cells from both technologies. In addition, we invest efforts in the design, synthesis and testing of catalysts for electrolyzers as part of our effort to work on large energy challenges. Work on effective catalysts and durable membranes for fuel cells in on-going.

The work toward these goals unifies all INREP groups in effective distribution of tasks, linked to the individual groups' capabilities.

In general, we continue in intensifying collaborations among all INREP groups. This report reflects well the integrity of this organization.

We hope to substantiate and formalize our relationship with the Moroccan scientists, and to establish running large bi-national energy project.

Executive summary

1. We suggest now optimal batteries and fuel cells for regular electric cars, drones and other unmanned vehicles. We can demonstrate selected systems. The progress is described in this report.
2. We develop important aspects of hydrogen economy: production, storage and effective use in fuel cells.
3. We also work on electrochemical technologies for large energy storage.
4. Despite the COVID19 pandemic world crisis, 2021 (like 2020) was a very prolific year for most INREP groups. The research in most laboratories never stopped even during lockdowns (by special arrangements and permissions). This report reflects a continuous progress.
5. During 2021 (like in 2020) we could not participate in regular international meetings and could not organized and conduct our own in-person annual INREP meeting.
6. INREP researchers also participated during this year in dozen of on-line meetings. The world international scientific communication moved world-wide from physical face-to-face meetings to on-line electronic conferences. Now we get back to regular international meeting in person.
7. We established be weekly seminar by Zoom for all INREP PIs which includes also discussions on crystallization of unique new INREP technologies. During the first half of 2022, our bi-weekly seminars were dedicated to analyze the work that was carried out by the various groups during 2021. All INREP groups presented their work and achievements during 2021during the seminars in January – June 2022.

Summary of 2021 Achievements – Batteries:

A major goal is to optimize high energy density Li metal and Li-ion batteries. We work on cathodes, anodes, electrolyte solutions, solid electrolytes, new characterization techniques. We also work on Li-S batteries, high specific capacity Si anodes for Li ion batteries.

Other goals relate to aqueous and non-aqueous rechargeable Na batteries (carbonaceous red-ox anodes, sodiated manganese oxide cathodes), rechargeable Mg and Zn batteries.

Go/No-Go decisions

- We concluded that Li-oxygen batteries are not relevant for the time-frame of INREP already during 2020 as we reported previously.
- We concluded work on conventional EDLC super-capacitors during 2020. In 2021 we went further and concluded work on pseudo-capacitors as well. We emphasize battery systems only as important and relevant power sources.
- We substantiate works on Li metal based batteries, Li-S batteries and development of solid electrolytes, mostly for Li metal based batteries.
- We substantiate work on solid state sodium batteries as well. We see synergism in working on both Li and Na batteries with active metal foils anodes and solid-state electrolytes.
- We substantiated the successful collaboration among Aurbach, Noked, Zitoun (BIU), Peled and Golodnitsky (TAU), working together on solid-state batteries. We have a consortium financed by BIRD (Israel – US) foundation and the DOE (USA) which includes the above groups from TAU & BIU + two Israeli start-up companies (Materials-Zone & 3DB) and the American partners which

include prominent research groups from the university of Maryland and SAFT (well known battery company).

- We continued to work on developing very effective novel surface treatments by several approaches including ALD (Ein-Eli, Noked) and exercised work with analytical tools for their probing, with an emphasis on solid state NMR (Leskes).
- We substantiated novel analytical work in which Terahertz (THz) time-domain-spectroscopy method is applied for the in-operando characterization of electrodes, interfacial phenomena and dynamics related to working lithium-ion battery prototype.
- We continued developing new doping processes and applied them for stabilizing several Ni rich NCM cathode materials, including the high specific capacity LNO containing 90% nickel (starting > 250 mAh/g , while charging < 4.3 V vs. Li)).
- We substantiate efforts to extract more capacity from conventional $LiCoO_2$ cathodes by charging them to 4.6V. We developed unique coating, binding and new electrolyte solutions for that. Work is in progress (in collaboration with ATL, China, the biggest Li ion battery producing company).
- We established a very intensive work on developing Na ion batteries for large energy storage, based on most abundant elements in earth crust.
- By an extension of our long-term collaboration with BASF, we developed during 2021 stable high voltage (4.8V) rechargeable batteries based on Li metal anodes and surface protected $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathodes.
- We extend INREP work to rechargeable Zn batteries and continue working on Mg batteries as well, emphasizing examination of new electrolyte systems and new cathodes based on VO_x active mass (which can intercalate reversibly Mg ions) , coated by protective sulfide layer which is compatible with electrolyte solutions in which Mg anodes behave reversibly. We also developed new effective anodes for rechargeable aqueous calcium batteries.
- We suggest strategical approaches, how to ensure the electrification of Israel from renewable energy sources, by outlining development of most effective large energy storage technologies based on rechargeable batteries and hydrogen economy. We believe that by a good organization we can ensure Israeli "green energy" independence, based on local production. We are involving Israel Chemicals Company (ICL) , Israel Electricity Company (IEC) and local start-up companies that can be up-scaled to become Israeli Battery Manufacturing Companies that can massively produce rechargeable batteries for large energy storage.

Major systems

Li-ion batteries

We completed development of high capacity Ni rich NCM cathodes $LiNi_xCo_yMn_zO_2$; $x \rightarrow 1$, x+y+z = 1, emphasizing work on $LiNiO_2$ (LNO) that can demonstrate initially a specific capacity approaching 270 mAh/g, upon charging up to 4.3 V vs. Li only. Major stabilization was reached by developing effective coating. We developed high capacity $Li_{1.14}Ni_{0.23}Co_{0.11}Mn_{0.52}O_2$ cathodes (Li & Mn rich NCM) stabilized by surface treatments with SO_2 and then with NH_3, that form passivated surface that avoid detrimental side reactions between solution species and the active mass. By collaboration with ATL China we demonstrate 4.4V Li ion batteries with LCO cathodes, charged to 4.6V that can reach practical energy density > 400Wh/Kg. A major progress was made in stabilization of high energy rechargeable Li-LCO cells through new surface treatments that affect both electrodes and the use of electrolyte solutions containing di-methyl carbonate (DMC), fluoro-ethylene carbonate (FEC), di-difluoro-ethylene carbonate (DFEC) and $LiPF_6$ as the Li-salt. We extended our work on new electrolyte solutions based on fluorinated organic co-solvents during 2021 by establishing a formal collaboration with the American company Koura which produces a variety of fluorinated organic solvents. We have on-going collaboration on these topics between the groups of Aurbach, Noked, Leskes, Ein-Eli, and the work is guided by computational work carried out by the group of Dan Major.

Novel Si anodes are further developed by Aurbach, Peled and Golodnitsky (on-going. work, supported by part by GM , USA).

We currently demonstrate full cells (developed by INREP) via our prototypes production line maintained by the ETV company, which facilities are at BIU.

Li metal based batteries with sulfur cathodes.

New sulfur cathodes (composite S – C, Li_2S – C, FeS_x) are currently developed by Aurbach, Peled and Golodnitsky. This is an on-going work which leads to develop of final battery concepts. An important decision here is the compromise between very high energy density (use of Li metal foils anodes, > 70% sulfur in the composite cathodes, minimal amount of electrolyte solution) and cycle life.

Protected Li anodes are developed by Ein-Eli, Noked, Aurbach, Peled & Golodnitsky, with computational guidance by Natan.

These high energy density battery systems are suitable mostly for electrical drones.

Li metal based batteries with solid electrolytes.

Solid electrolytes and solid-state battery systems are developed by Golodnitsky, Peled, Aurbach, Zitoun and Noked in a joint Israel – US project supported by the BIRD foundation and the DOE.

Rechargeable Na ion batteries.

We established a new project which develops Na ions batteries for large energy storage, by Noked & Aurbach groups, supported by the Israeli energy company Dor-Al.

Rechargeable Mg batteries

Noked, Eineli and Aurbach groups belongs to a European consortium called E-Magic, supported by the European Commission. The consortium is manage by the strong Spanish R&D company CIDETEC, includes also research groups from Spain, France, Germany, Denmark and the U.K. This consortium has reached the most impressive progress so far, in developing nearly practical rechargeable Mg batteries (including prototypes demonstration by CIDETEC, Spain and CEA, France). During 2021, we explored very intensively surface phenomena related to the electrolyte solutions that are considered as the most promising for these systems. We discovered some annoying issues related to unavoidable side reactions that lead to a serious doubt on the chance to ever reach with Mg battery systems the necessary high cycling efficiency (should approach 100%), which is mandatory for advanced rechargeable batteries.

Rechargeable Zinc Batteries.

During 2021, Mandler and Aurbach groups established collaboration on Zn – Br stationary batteries for large energy storage, supported by part by the Ministry of Energy.

Unique analytical capabilities.

We continue to develop *in-situ* techniques for the characterization of batteries electrodes using EQCM-D in conjunction with *in-situ* AFM on the same systems (Aurbach), multi-nuclei solid-state NMR (Leskes, Aurbach), Simultaneous AFM-

SECM-TERS on single particles (Schechter), Tera-Hertz spectroscopy (Fleischer, Peled, Golodnitsky), on-line mass spectroscopy (Noked), *in-situ* electron microscopy (Ein-Eli). In addition to intensive analytical work including all kinds of electrochemical, spectroscopic and microscopic techniques.

Computational and theoretical work.

We continue to develop computational capabilities that enable design of new cathode materials for advanced Li-ion batteries (Major). Work on doped Ni rich NCM cathode materials for high energy density Li ion batteries is already guided by this computational work. We also develop computational work for the analysis and design of active surfaces (Natan). We develop novel analyses for electrochemical impedance spectroscopy of composite electrodes and fuel cells degradation (Tsur).

Practical aspects.

We are testing thousands of batteries prototypes per year. These include Li, Li ion, Na, Na ion aqueous and non-aqueous batteries, nonaqueous Mg batteries and preliminary aqueous Zn and Ca battery models.

Next steps and further decisions

1. We continue successful work on high energy Li-S batteries but we are giving -up development of Li-Si-S.
2. We will continue work on high specific capacity Li & Mn rich NCM cathodes, through collaboration between Aurbach (synthesis) and Eineli (protective coating by ALD.
3. We will continue our work on 4.8V Li-ion batteries based on graphite anodes and $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathodes, moving to practical realization in pouch cells (through collaboration with BASF).
4. We will continue work on high voltage/high capacity $LiCoO_2$ cathodes for conventional Li ion batteries, moving to demonstration of up-scaling of processes that we developed.
5. We intensify work on rechargeable nonaqueous Na ion batteries for large energy storage. We established relationship with the Czech company Bochemie-GAZ, which produces Ni-Cd batteries for load leveling applications. They want to take part in our efforts to develop Na ions batteries.
6. We continue work within INREP on other batteries for load-leveling and large energy storage applications. This includes rechargeable zinc batteries (Aurbach), flow batteries (Zitoun, Suss) and aqueous sodium batteries.
7. We will suggest holistic solutions for the massive electrification of Israel by solar energy, by a combination of hydrogen economy and rechargeable batteries (deserves an extensive discussion, beyond the scope of this report).
8. The groups of Avner Rothschild and Gideon Grader from the Technion who developed a practical approach to produce hydrogen (established successfully their H2-Pro company), joined INEP. We expect to accelerate work on "green" hydrogen production by electrochemical means and promote development of hydrogen economy in Israel for both electromobility and large energy storage & conversion.

Important note: the extension of INREP in terms of number of groups involved, means a gain in experience and performance, enabling us to broaden our scope of work, without jeopardizing quality.

Summary of 2021 Achievements – Fuel Cells:

Durability

- Increase in the surface area of WC by an order of magnitude to allow their utilization as catalyst support in PEMFCs.
- Incorporation of N, B, and S dopants in carbon supports to increase the corrosion resistant of the supports.
- Fuel cell testing with ceramic supports.
- Elucidating the degradation mechanisms of PGM-free catalysts in PEM and AEM fuel cells.
- Development of durable and highly active PGM-free OER catalysts based on NiFeTiOOH
- Development of TiNC supports for fuel cells.
- CeO_2 enclosed by N-doped carbon, derived from porphyrin polymers provides an onsite scavenging of peroxides formed during oxygen reduction at the cathode
- new Pt free βAg2Se exhibit high ORR activity and stability in alkaline conditions as well as spinel nickel ferrite on MoS2 as bifunctional ORR/OER catalysts for regenerative FCs.
- Magnetron sputtering of Ta onto a carbide-based electrode can simultaneously improve its oxygen reduction activity and durability under accelerated stress testing. This improvement came from a protective Ta_2O_5 phase which both prevented Mo_2C oxidation and micro-void formation at the electrode-membrane interface
- Electrodeposition of Pt onto Mo_2C nanoparticles could be used to synthesize low-dimensional Pt nanostructures (<2nm) with superior metal-support interactions. In order to exploit this advantage, the deposition needs to occur within a specific electrochemical window ~100 mV wide. Deposition above this window will not allow for nuclei formation (growth still possible) and deposition below this window will cause the deposition mechanism to shift to larger 3D structures. Improved Pt-Mo_2C interfaces also showed improvements to mass activity and the ability to maintain a stable surface area after significant electrochemical cycling.
- We showed how alloying Mo_2C with TaC gave rise to a catalyst support which was simultaneously more active and more stable as an anode in alkaline fuel cells. The improved activity was demonstrated by showing how allowing Mo_2C with other transition metal carbides can modulate the electronic structure of PtRu (EXAFS), as well as DFT calculations showing "volcano plot" behavior where the hydrogen binding energy varied as a function of alloying carbide. This is a relatively new strategy in the AFC world since the majority of studies try to boost activity by modulating the metal catalyst structure – where instead we show that it is possible to achieve this goal by modulating the support phase
- Showed that oxynitride phases are durable supports for NiFe nanoparticles at a direct-ammonia solid-oxide fuel cell (SOFCs)
- Optimized AEMs, by functionalizing with novel isoindolinium FGs and obtained membranes that are superior to existing commercial. Best results in

alkaline fuel cell tests were obtained by connecting isoindolinium to HDPE backbones. We have patented this new FG.

- Corrosion tolerant HBr redox-flow battery
- We developed new methods to measure electrooptical losses in transition metal oxide photoelectrodes for photoelectrochemical water splitting.
- We discovered that hematite (iron oxide) photoanodes for photoelectrochemical water splitting lose about half of the absorbed photons for localized d-d electronic transitions that do not generate electron-hole pairs, solving a half-century old enigma and revealing the cause of underperformance of hematite photoanodes.

Activity

- Development of aerogels based on transition metal complexes for ORR. Increased the active site density by a factor of 5 in order to raise performance. This was done with porphyrins, phthalocyanines and corroles and their combinations.
- Development of a new class of PGM-free ORR catalysts: porphyrolles, which allow the directed synthesis of bi-metallic catalysts frameworks.
- Set the state of the art in PGM-free OER electrocatalysis in AEM electrolyzers. Presented at the US-DOE AMR.
- Developed of the first active metal-free OER catalyst using combination of machine learning, AI and experimental work.
- Developed Ni and NiFe aerogels to increase catalyst utilization and raise overall performance in AEM electrolyzers.
- Developed of NiFeCoOOH OER catalysts.
- Developed a high density liquid hydrogen carriers
- Developed a new direct liquid hydrogen fuel cell, which out performs DMFCs by a factor of 3 in peak power.
- Simulation of ORR reactions at metal surfaces
- Improved deep learning based MD
- We have studied and developed Metal-free oxygen reduction reaction (ORR) catalysts of ultra-low cost and high catalytic activity for affordable anion exchange membrane fuel cells (AEMFCs).
- Modeled the catalyst activity using the first principal density functional theory (DFT) calculation to shed light on the intrinsic kinetic activity .
- We succeed to develop bi-functional doped graphites (I- , S-, N- and B-doped-graphite) as a metal-free catalyst for the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) in alkaline electrolytes. The doped graphites showed promising AEMFC performance indicating their potential as cathode catalysts in AEMFCs .
- First direct ammonia HT-AEMFCs coupled with PGM-based catalysts was successfully tested at a cell temperature of 8 °C and 100°C. At elevated cell temperature (100°C), the peak power density and limiting current density were significantly improved .
- OCV increases from 0.5V to 0.75V when the cell temperature goes from 80°C to 100°C, indicating the promising benefit from high temperature operating conditions.

- We presented the first 1-D and transient model of AEMFC operated with ammonia fuel, capturing species transport within the cell as well as significant electrochemical reactions taking place in the cell. The model predictions are in good agreement with the experimental data .
- Recently studied the temperature effect on hydroxide diffusion in anion exchange membranes (AEMs). It was found that the OH− diffusion changes non-monotonically with increasing temperature. Discovery of this unusual temperature dependence of the diffusivity will play an important role in the design of new, stable, highly conducting AEM fuel cell devices.
- Oxynitrides are synthesized themselves in ammonia and are therefore prime candidates for stable materials under DA-SOFC anode conditions. Power density of nearly 300mW/cm^2 at 700°C, one of the highest reported for 100μm YSZ electrolyte-supported cells. Oxynitride supports degrade at a slower rate compared to their YSZ counterparts. (under review in JMCA)
- We developed and patented a thermochemical ammonia synthesis catalyst which outperforms nearly every competing material in the literature, particularly given its low Ru loading. (manuscript under preparation, patent submitted)
- We developed and patented a multiphase molten metal catalytic reactor for methane pyrolysis reactor for turquoise hydrogen generation. (manuscript under preparation, patent submitted)
- We developed a unique system with high sensitivity and high accuracy for spectral quantum efficiency measurements of photoelectrochemical solar cells.
- We discovered an unusual light-bias effect on the quantum efficiency spectrum of $BiVO_4$ photoanodes for photoelectrochemical water splitting.
- We developed carbon cloth supported nickel (oxy)hydroxide electrodes for E-TAC water electrolysis with superior performance compared to electrodes on nickel foam substrates.
- Develop new catalysts for urea oxidation based on non-noble metals based on oxides or molecular organo-metallic complexes
- Understanding the instability mechanism of ammonia oxidation on copper-based catalyst in alkaline electrolytes
- Develop low Pt anode catalysts loading for DME, Methyl formate methanol and their mixture in high power direct gas fed fuel cells. Elucidation of the reaction mechanism steps of these anodic reactions using DFT and selected sector-electrochemical methods .
- Energy storage - Studying the reduction of N2 to ammonia on selected synthesized catalysts materials and various electrolytes .
- We extended our work on preparation of highly conductive electrospun PEMFC membranes with through-plane conductive channel-orientation to optimize Nafion:PVDF ratio for maximal conductivity .
- We developed a new procedure for thermally induced controlled fusion of Nafion-PVDF nanofiber composite to overcome membrane durability problems found during testing at Prof Elbas's lab (BIU). This procedure is implemented in a new fusion process and setup for preparing membrane with improved integrity.
- We introduced and implemented improved measurement setup and protocols for overcoming the challenge of accurately assessing ultra-low through-plane conductivity, highly important for understanding composites with anisotropic

characteristics. We also combined the measurements with SAXS and 3D swelling to assess anisotropcity of structure, conductivity and swelling of such composites.

- We collaborated with Prof Dekel's group (Technon) in developing novel electropolymerized ultra-thin anion-conducting membranes and the use of impedance spectroscopy for their characterization.
- We collaborated with Prof Frei group (Mat Sci & Eng, Technion) on chearacterization novel materials with mixed electronic-ionic conductivity using electrochemical QCM.
- In collaboration with Prof. Ulbricht's group (Essen, Germany), we developed novel Nafion-polyamine composite membrane for improved mono-/divalent ion selectivity. We employed this novel material to unravel ion transport mechanism in polyelectrolyte complex membranes.
- We also develop new models for ion transport in ion-conducting materials in collaboration with Prof Nit (BGU)

Bar Ilan University

Doron Aurbach's group

Doron Aurbach's group in 2021 (people related to INREP)

Mikael Levi	Prof	Boris Markovsky	Prof.
Netanel Shpigel	PhD, Senior researcher (by part)	Elena Markevich	Prof.
Gregory Salitra	Prof.	Nofar Tubul	MSc student
Yosi Gofer	PhD	Yehudit Grinblat	PhD
Nicole Leifer	PhD	Miri Grinstein	PhD
Shalom Luski	PhD	Hadar Sclar	Postdoc
Sandipan Meiti	Postdoc	Francis Amalraj	Postdoc
Tirupathi Rao Penki	Postdoc	Hadas Alon-Yehezkel	Postdoc
Satya Narayana	Postdoc	Gil Bergman	MSc student
Tianju Fan	Postdoc	Bar Gavriel	PhD student
Ben Delugatch	PhD student	David Lustig	PhD student
Elad Ballas	MSc student	Naresh Vangapally	Postdoc.
Shaul Bublil	PhD student	Meital Turgeman	PhD student
Harika Vila	Postdoc	Gayathri Peta	Postdoc.
Ortal Raskin	PhD student		

The group of Doron Aurbach made progress in the following areas during 2021:

1. We developed new Ni rich cathode materials for high energy density Li ion batteries with Ni concentration around 90% Ni (220 mAh/g), stabilized by two dopants – B & Mo. We completed extensive work on dopants for these systems aided by computational work (in collaboration with Dan Major's group).

2. We enlarged our work on new electrolyte solutions for advanced rechargeable Li batteries, which contain fluorinated co-solvents. We completed mechanistic studies related to solutions containing both FEC and DFEC. We established collaboration with Koura, USA, which develops new fluorinated solvents. We demonstrated advantages for at least 3 new fluorinated solvents. Work is in progress.
3. We demonstrated that we can stabilize $LiCoO_2$ – LCO cathodes charged to 4.6 V, delivering 220 mAh/g, by developing unique coating and using electrolyte solutions with fluorinated co-solvents that develop protective surface films on the electrodes. In a very intensive study we demonstrated the limitation of the most important redox mediators suggested in the literature for Li-oxygen cells and in fact stopped our work on these systems.
4. We developed another type of high capacity cathode for on high energy density Li ion batteries with the stoichiometry $Li_{1.14}Mn_{051}Ni_{0.23}Co_{0.12}O_2$, can deliver > 250 mAh/g, stabilized by double gas treatments SO_2 and then NH_3 at elevated temperatures.
5. We demonstrated stabilization of high voltage $LiMn_{1.5}Ni_{0.5}O_4$ cathodes by surface treatments based on layered compounds that are adsorbed to the active mass surface and form buffer zones that mitigate detrimental dissolution of Ni and Mn ions.
6. We developed new organic anodes for aqueous rechargeable batteries based on multivalent metal cations (demonstrated with Ma, Ca, Mg), based on organic polymers with reversible red-ox axtivity. b
7. We examined new electrolyte solutions and new red-ox polymer cathodes for rechargeable Mg batteries.
8. We started a new project aiming at developing nonaqueous Na ion batteries for large energy storge (together with Noked group, supported by the Israeli company Dor-Al).
9. We continued our on-going efforts to develop high energy density rechargeable Li-S batteries which are simple, safe and very cost-effective.
10. We started working on rechargeable stationary Zn-Br batteries.
11. We are developing composite solid electrolytes for Li and Na batteries, comprising ion conducting polymeric matrices + Li and Na conducting ceramic particles. We demonstrated progress via systematic work.
12. On the analytical side: we are making a further progress with EQCM-D based methodologies for evaluating composite intercalation electrodes. We developed further capabilities to study Na and Li insertion electrodes using solid-state NMR.

<u>Collaborations</u>

During 2021 we maintained vital collaborations with the following industries:

1. BASF (Germany)
2. GM (USA)
3. Nichia (Japan
4. Collaboration with ATL China, the biggest Li ion batteries manufacturer in the world.
5. We established new collaboration with Koura (USA) which develops new fluorinated organic solvents.

6. We have academic collaborations with the groups of Martin Winter, Yang-Kook Sun (Hanyang university (S. Korea), Yury Gogotsi (Drexel university, USA).
7. A formal collaboration with the group of Prof. Nae-Lih Wu in Taiwan.
8. We have a collaboration on energy storage materials with the group of Prof. Yan Xiang, Beihang University, Beijing, China.
9. We are part of a new European Consortium E-Magic which includes the groups of Ein- Eli and Noked from Israel + groups from Spain, Germany, France, Denmark and the UK, developing rechargeable Mg batteries.
10. We have on-going collaboration through USA – Israel consortium supported by the BIRD foundation and the DOE - USA which explore solid electrolytes and develop solid-state batteries together with two INREP groups from BIU, two INREP groups from TAU, several Israeli and American start-up companies and research groups in the University of Maryland USA.

Within INREP we have collaborations now with Yair Ein Eli, Malachi Noked, David Zitoun, Dan Major, Zeev Gross, Dina Golodnitsky, Dan Mandler and Emanuel Peled. Our work is very well documented in relevant papers during 2020.

Publications in 2021 (related to the INREP activities):

(1) Maddukuri, S., Nimkar, A., Chae, M. S., Penki, T. R., Luski, S., & Aurbach, D. $Na_{0.44}MnO_2$/polyimide aqueous Na-ion batteries for large energy storage applications. *Frontiers in Energy Research* **2021**, *8*.

(2) Bublil, S., Leifer, N., Nanda, R., Elias, Y., Fayena-Greenstein, M., Aurbach, D., & Goobes, G. Alumina thin coat on pre-charged soft carbon anode reduces electrolyte breakdown and maintains sodiation sites active in Na-ion battery–Insights from NMR measurements. *Journal of Solid-State Chemistry* **2021**, *298*, 122121.

(3) Breddemann, U., Sicklinger, J., Schipper, F., Davis, V., Fischer, A., Huber, K., ... & Krossing, I. Fluorination of Ni-Rich Lithium-Ion Battery Cathode Materials by Fluorine Gas: Chemistry, Characterization, and Electrochemical Performance in Full-cells. *Batteries & Supercaps* **2021**, *4*(4), 632-645.

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Special Achievements of the group during 2021

1. Belonging to the group of highly cited scientists by Clarivat Analytical and W.O.S.

2. Published 35 papers in 2021, cited 8485 times (W.O.S) and nearly 9800 (Google Scholar) during 2021 alone. In July 2022, H-indices 128 (W.O.S), 143 (Google Scholar), more than 70000 and 88100 total citations (from the two sources, respectively).

3. Received the gold medal of the Israel Chemical Society (for 2020, ceremony in 2021).

4. Ranked as # 89 in Chemistry, and as # 133 in Materials Science in the world, ranked as # 2 in Israel on both areas, published by: a group called "Research.Com" which is related to several US universities.

Also ranked among top 500 scientists in the world, second in Israel (all fields of science, out of top 2% scientists), published by a group from Stanford university.

5. 5 people completed their PhD work during 2021, submitted theses.

<u>Presentations in international meetings/Events</u>

The world transportation has changed and contracted considerably due to the COVID19 pandemic crisis. Hence, international conferences moved from a face-to-face mode to an on-line electronic modes: from Seminars to Webinars.

We participated during 2021 in at least 20 international meetings by ZOOM.

These included lectures to teams at ATL, Koura, Nichia and E – Magic consortium on Mg batteries and Mg electrochemistry.

<u>List of grants:</u>

1. Industrial grants (during 2021): BASF (Germany) 200K Euros p.a., GM (USA) 150K USD p.a., Nichia (Japan) 120K USD p.a. Koura (USA) 100K USD, p.a.
2. Developing Na ion batteries for large energy storage (collaboration with Noked group), Dor-Al (Israel), 500K USD
3. Developing cells for hydrogen production Dor-Al (Israel) 60K USD.
4. Ministry of Energy, Israel – a project related to large energy storage.
5. ISF – a new one on solid-state batteries, a new project started Oct. 2019, 80K USD p.a.
6. Ministry of Science & Technology (MOST) – 2 Israel-Germany projects on Mg-S batteries and on multivalent metal anodes based batteries.
7. MOST – Israel-Taiwan on SS batteries, 50K USD p.a.
8. EC project: E. Magic consortium targeting on developing rechargeable Mg batteries (4 Israeli groups, 2 Spanish groups, groups from Germany, France, Denmark, UK), 120K Euros p.a.
9. Working in the framework of a new Israeli-American consortium supported by BIRD foundation and DOE (USA), including 3 groups at BIU, 2 groups at TAU (all of them are INREP members), several Israeli and American start-up companies and a group of researchers from the university of Maryland USA (5 years, 120K USD per group per year).

<u>Work planned to 2022-2023:</u>

We will continue to work on advanced Li ion batteries.

New Si containing high specific capacity anodes (collaboration with GM, USA).

4 types of cathodes: $LiMn_{1.5}Ni_{0.5}O_4$ 5V spinel (emphasis on solutions additives, collaboration with BASF, Germany) ; $LiNi_{90}Co_{0.5}Mn_{0.5}O_2$ with two dopants: B & Mo, and $Li_{1.14}Ni_{0.23}Co_{0.11}Mn_{0.52}O_2$ (emphasis on effective coatings by ALD processes, developed by Eineli group) , LCO (collaboration with ATL, China, emphasis on taking the material used by ATL , beyond the state of the art, reaching stable 220 mAh/g by charging to 4.6V, demonstrating up-scaling capabilities).

We will continue to work on fluorinated solutions for advanced Li ion batteries by collaboration with Koura, USA.

We will work intensively on developing Na ion batteries for large energy storage, in collaboration with Noked group at BIU, and the companies Dor-Al and Bochemie-GAZ.

We will continue working on aqueous Ca and Mg batteries via developing anodes based on polymeric red-ox materials that can interact reversibly with multivalent metal cations.

Aurbach & Noked groups started working on rechargeable Zn-air batteries, in collaboration with Nichia, Japan. will continue to work on grafted high capacity activated carbon and carbonaceous red-ox active electrodes for aqueous sodium ion batteries

We will continue to optimize Li-S battery systems, emphasizing very high energy density and low cost on the account of prolonged cycling).

We will continue our on-going work on Mg batteries in collaboration with the groups of E-Magic consortium (an EC project), emphasizing solutions based on the solvent DME and the salt Mg-di [tetra (hexafluoro-isopropyl) borate] – $Mg[B(HFIP)_4]_2$. These solutions enable reversible Mg deposition in chlorides (Cl^-) free solutions. They may have high anodic and cathodic stability, enabling to develop high voltage/high energy rechargeable Mg batteries with magnesiated transition metal oxide cathodes (e.g. Mg_xVO_y compounds). There are a lot of aspects to explore, in order to ensure full reversibility (approaching 100%) of Mg metal anodes in them.

Lior Elbaz's group

Current Team Members working on FC related projects (not only in the framework of the IFCC):

First Name	Last Name
Oran	Lori
Ariel	Friedman
Noam	Zion
Wenjamin	Moschkowitch
Leigh	Peles
Rafi	Snitkoff

Hilah	Honig
Yan	Yurko
Alisa	Kozhushner
Yeela	Perskey
Or	Rimon
Michal	Mizrahi

Research Topic/s:

1) Catalysts development for AEMFCs and PEMFCs;
2) Development advanced corrosion-resistant supports for PEMFCs.
3) Development of testing methodologies for PEMFCs
4) Development of OER/HER catalysts
5) Development of hydrogen carriers
6) Development of advanced fuel cells technologies (new ones)

Ultimate Research Goals in the Framework of the IFCC:

1) Highly active ORR PGM-free catalysts for PEMFCs
2) Highly durable PEMFCs
3) Development of AEM electrolyzers based on PGM-free catalysts

Relevant Instrumentation in your lab:

1) RRDE systems
2) BET
3) Mass spec – directly connected to FC stations
4) FC test stations
5) EL test stations
6) SonoTek spray system for MEA fabrication
7) XRF
8) FTIR-ATR

Major Achievements for FY2021:

1) Increase in the surface area of WC by an order of magnitude to allow their utilization as catalyst support in PEMFCs.
2) Incorporation of N, B, and S dopants in carbon supports to increase the corrosion resistant of the supports.
3) Fuel cell testing with ceramic supports.
4) Elucidating the degradation mechanisms of PGM-free catalysts in PEM and AEM fuel cells.
5) Development of durable and highly active PGM-free OER catalysts based on NiFeTiOOH
6) Development of TiNC supports for fuel cells.
7) CeO_2 enclosed by N-doped carbon, derived from porphyrin polymers provides an onsite scavenging of peroxides formed during oxygen reduction at the cathode

8) Development of aerogels based on transition metal complexes for ORR. Increased the active site density by a factor of 5 in order to raise performance. This was done with porphyrins, phthalocyanines and corroles and their combinations.
9) Development of a new class of PGM-free ORR catalysts: porphyrolles, which allow the directed synthesis of bi-metallic catalysts frameworks.
10) Set the state of the art in PGM-free OER electrocatalysis in AEM electrolyzers. Presented at the US-DOE AMR.
11) Developed of the first active metal-free OER catalyst using combination of machine learning, AI and experimental work.
12) Developed Ni and NiFe aerogels to increase catalyst utilization and raise overall performance in AEM electrolyzers.
13) Developed of NiFeCoOOH OER catalysts.
14) Developed a high density liquid hydrogen carriers
15) Developed a new direct liquid hydrogen fuel cell, which out performs DMFCs by a factor of 3 in peak power.

Go/no-Go points:

1) n/a

Plans for FY 2021 (please relate to the US DOE bench marks and goals):

1) Development of in-operando methods to study PGM-free degradation in PEM and AEM fuel cells.
2) Synthesize and study 3D scaffolds of well-defined ORR catalysts with improved mass transfer.

Which components developed in your lab in recent years can be implemented in a fuel cell today (also include scale in size and weight when relevant):

1) Ceramic supports based on Mo2C, WC, TiNCand TiC
2) Molecular ORR catalysts based on polycorroles
3) PGM-free ORR catalysts based on aerogels (patented)
4) Optimized MEA fabrication capabilities for a variety of systems.
5) Understanding of degradation mechanisms in of cathode and catalytic materials.
6) New direct liquid hydrogen carrier fuel cell

Relevant Publications FY2021:

1) Assessing and Measuring the Active Site Density of PGM-free ORR Catalysts (R. Snitkoff-Sol and L. Elbaz, Journal of Solid State Electrochemistry, 2022, Accepted).
2) Electrocatalysis of Oxygen Reduction Reaction in Polymer Electrolyte Fuel Cell with Covalent Framework of Iron Phthalocyanine Aerogel (N. Zion, L. Peles-Strahl, A. Friedman, D. Cullen, L. Elbaz, ACS Applied Energy Materials, 2022, Accepted.(
3) What is next in anion-exchange membrane electrolyzers? Bottlenecks, benefits, and future (C. Santoro, A. Lavacchi, P. Mustarelli, V. Di Noto, L.

Elbaz, D. Dekel, and F. Jaouen, ChemSusChem, 2022, 15, e202200027). https://doi.org/10.1002/cssc.202200027

4) Quantifying the Electrochemical Active Site Density of PGM-free Catalysts in-situ Fuel Cells using Fourier Transform Alternating Current Voltammetry (R. Z. Snitkoff-Sol, A. Friedman, H.C. Honig, Y. Yurko, A. Kozhushner, M. J. Zachman. P. Zelenay, A. Bond, and L. Elbaz, Nature Catalysis, 2022, 5, 163-170). https://doi.org/10.1038/s41929-022-00748-9
5) Recent Progress and Viability of PGM-free Catalysts for Hydrogen Evolution Reaction and Hydrogen Oxidation Reaction (W. Moschkowitsch, O. Lori, L. Elbaz, ACS Catalysis, 2021, 1082-1089). https://doi.org/10.1021/acscatal.1c04948
6) Application of Molecular Catalysts for Oxygen Reduction Reaction in Alkaline Fuel Cells (A. Friedman, M. Mizrahi, N. Levy, N. Zion, M. Zachman, L. Elbaz, ACS Applied Materials & Interfaces, 2021, 13, 49, 58532-58538). https://doi.org/10.1021/acsami.1c16311
7) 3D Metal Carbide Aerogel Network as Stable Catalyst for the Hydrogen Evolution Reaction (O. Lori, N. Zion. H. C. Honig, and L. Elbaz, ACS Catalysis, 2021, 11, 13707-13713). https://doi.org/10.1021/acscatal.1c03332
8) The Effect of Membrane Electrode Assembly Methods on the Performance in Fuel Cells (Y. Yurko and L. Elbaz, Electrochemica Acta, 2021, 389, 138676-138681). https://doi.org/10.1016/j.electacta.2021.138676
9) Bipyridine Modified Conjugated Carbon Aerogels as a Platform for the Electrocatalysis of Oxygen Reduction Reaction (L. Peles-Strahl, N. Zion, O. Lori, N. Levy, G. Bar, A. Dahan and L. Elbaz, Advanced Functional Materials, 2021, 2100163). https://doi.org/10.1002/adfm.202100163
10) Porphyrin Aerogel Catalysts for Oxygen Reduction Reaction in Anion-Exchange Membrane Fuel Cells (N. Zion, J.C. Douglin, D.A. Cullen, P. Zelenay, D.R. Dekel and L. Elbaz, Advanced Functional Materials, 2021, 2100963). https://doi.org/10.1002/adfm.202100963
11) Control of Molecular Catalysts for Oxygen Reduction by Variation of pH and Functional Groups (A. Friedman, N.R. Samala, H.C. Honig, M. Tasior, D.T. Gryko, L. Elbaz and I. Grinberg, ChemSusChem, 2021, 14 (8), 1886-1892). https://doi.org/10.1002/cssc.202002756
12) Durable Tungsten Carbide Support for Pt-based Fuel Cells Cathodes (O. Lori, S. Gonen, O. Kapon, L. Elbaz, ACS Applied Materials & Interfaces, 2021, 13 (7), 8315-8323). https://doi.org/10.1021/acsami.0c20089
13) Optimization of Ni-Co-Fe based catalysts for oxygen evolution reaction by surface and relaxation phenomena analysis (R. Attias, K.V. Sankara, K. Dhaka, W. Moschkowitsch, L. Elbaz, M. Caspary-Toroker, Y. Tsur, ChemSusChem, 2021, 14 (7), 1737-1746). http://doi.org/10.1002/cssc
14) Bifunctional PGM-Free Metal Organic Frameworks-based Electrocatalysts for Alkaline Electrolyzers: Trends in the Activity with Different Metal Centers (W. Moschkowitsch, S. Gonen, K. Dhaka, N. Zion, H. Honig, Y. Tsur, M. Caspary-Toroker, L. Elbaz, Nanoscale, 2021, 13, 4576-4584). https://doi.org/10.1039/D0NR07875A
15) Heterogeneous Electrocatalytic Reduction of Carbon Dioxide with Transition Metal Complexes (A. Friedman and L. Elbaz, Journal of Catalysis, 2020, 395, 23-35). https://doi.org/10.1016/j.jcat.2020.12.004
16) Methods for Assessment and Measurement of the Active Site Density in PGM-free ORR Catalysts (A. Kozhushner, N, Zion, and L. Elbaz, Current

Opinions in Electrochemistry, 2021, 25, 100620-100630).
https://doi.org/10.1016/j.coelec.2020.08.002

Presentations at Conferences 2020:

1) Invited talk at the 241st Electrochemical Society Meeting, Vancouver, Canada, May 30th, 2022.
2) Keynote talk at the Israelectrochemistry Meeting, Ariel University, Israel, May 26th, 2022.
3) Invited talk at the Green Hydrogen Open Day, Yotveta, Israel, March 10th, 2022.
4) Invited talk at the Research and Innovation Center on CO_2 and Hydrogen (RICH) seminar, Khalifa University, UAE, February 28th, 2022.
5) Invited talk and hydrogen economy panel member at the Eilat-Eilot Renewable Energy Conference, Eilat, Israel, December 16th, 2021.
6) Invited talk at the Israeli Materials Engineering Conference 2021 (IMEC2021), Jerusalem, Israel, December 13th, 2021.
7) Invited talk at the Italy-Israel Strategic Dialogue on "Italy and Israel: Facing Uncertainties, Overcoming Challenges", Virtual, September 30th, 2021.
8) Keynote lecture at the annual meeting of the Chemistry Society of Italy (SCI2021), Italy (virtual meeting), September 21st, 2021.
9) Invited talk at the National Fuel Cell Research Center (NFCRC), University of California at Irvine (UCI), Irvine, CA, US, July 23rd, 2021.
10) Invited talk at the 239th ECS meeting, Virtual, June 2nd, 2021.
11) Invited talk at the Digital Round Table: Hydrogen in Bavaria and Israel, Virtual
12) Workshop, April 27th, 2021.
13) Keynote lecture at the Italian Fuel Cells Workshop (IVWFC), Virtual workshop, March 18th, 2021.
14) Invited talk at the BIU-KU Workshop on Sustainable Energy, Robotics and Cyber, Virtual Workshop, February 9th, 2021
15) Invited talk at the 2nd NL-IL Mini-Symposium on Hydrogen and Renewable Energy, Virtual Seminar, February 2nd, 2021.

Grants 2021:

2022: Development of fuel cell-operated drones ($150K; Funding Agency: Israeli Ministry of Defense through **MAFAT**). PI: Lior Elbaz together with HevenDrones.

2022-2025: Elucidating the degradation mechanism of PGM-free ORR catalysts for fuel cells ($220K; Funding Agency: Israeli Ministry of Energy (**MOE**)). PI: Lior Elbaz.

2022-2025: Aerogels'-based catalysts for hydrogen generation in electrolyzers (($220K; Funding Agency: Israeli Ministry of Energy (**MOE**)). PI: Maytal Caspary-Troker (Technion, Co-PI: Lior Elbaz.

2022-2025: 3D Tunable Heterogeneous Molecular Catalysts Based on Porous Aerogels ($375K; Funding Agency: Israel Science Foundation (**ISF**)). PI: Lior Elbaz

2020-2023: Electropolymerization of metallo-corroles: Molecular catalysts for Fuel Cells ($200; Funding Agency: Israeli Ministry of Energy (**MOE**)). PI: Lior Elbaz.

2020-2022: Development of aerogels-based catalysts ($30K; Funding Agency: MIT Seed Funds – **MISTI**). PIs: Lior Elbaz (Israel) and Yogesh Surendranath (USA)

2019-2023: Corrosion Resistant Catalysts and Supports for Low-Temperature PEM Fuel Cell Cathodes ($350K; Funding Agency: Israeli Ministry of Science (**MoS**)). PI: Lior Elbaz in collaboration with Prof. Peter Strasser (TU Berlin; separately funded by **BMBF**)

2018-2022: Advanced non-Precious-Metal-Group Electrocatalysts for Fuel Cells ($340K; Funding: Israeli Science Foundation (**ISF**)). PI: Lior Elbaz.

Other activities:

2018-present: Member of the international forum of fuel cells consortia leaders (5 leaders from the US, France, Germany, Japan and Israel).

2017-present: Appointed as case expert on non-precious metal catalysts for fuel cells for the International Energy Agency Advanced Fuel Cells Annexes.

2017-Present: Israel's official representative at the International Energy Agency's Advanced Fuel Cells Executive Committee.

Summary of work

The two top hurdles in fuel cells technology today are durability and cost. Durability, as the US-DOE describes it, is the biggest hurdle. The Elbaz lab has been developing new, advanced materials, mostly based on porous, high surface-area, conductive ceramic materials which show significant durability when compared to the common carbonaceous materials used today. They are also developing methodologies to study corrosion in fuel cells, by studying the material's strengths and weaknesses and exposing them to extreme, yet realistic, operating conditions to simulate degradation which occurs over several years in only a few days. These projects are currently applied by his industrial partners. The Elbaz lab is also developing catalysts, mainly for oxygen reduction, based on ultra-low loading Pt. He is also developing biomimetic non-precious metal group catalysts based on relatively new and exciting transition metal complexes: metallo-corroles and three dimensional Pt-free catalysts. These are considered today to be among the state-of-the-art molecular catalysts for oxygen reduction.

During the last year, Lior's group has taken several approaches. The first is the design and synthesis of all-in-one aerogel cathodes for fuel cells. In this work, a novel approach to the synthesis and design of fuel cell electrodes is used. The electrode and catalysts are treated in a synergetic approach that will enable the development of both components in tandem. This approach introduces a high surface area, open pore structure, aerogel that will offer tunable chemical and physical properties. 3D catalytic structures with high catalytic site density were synthesized in a fine controlled manner, to allow control of mass transfer. These novel structures show enhanced activity in the catalysis of the oxygen reduction reaction (ORR) due to the synergism between catalytic sites which lower the over potential required for this reaction by more than 400 mV when compared to the porphyrin itself, making it comparable to Pt-based catalysts, hence, potentially removing the dependence on precious metals in fuel cells.

Another approach was taken by designing new and exciting molecular catalysts: metallo-corroles. Lior's group thoroughly studied this new class of catalysts for ORR, which include the study of the reaction mechanism and kinetics, thermodynamics, molecular and mechanistic modelling, and testing under real operating conditions, through the modification of the metal center and substituents. The most active metal center was found to be cobalt, whereas the effect of the substituents was found to be on the electron density around the metal. The addition of electro-withdrawing substituents resulted in lowering the activation energy for this reaction, and transition from the less desired 2-electron reduction to peroxide, to the favourable 4-electron reduction to water. These catalysts show the best activity. To further enhance its activity and the product yield of water from the ORR, we electropolymerized these molecular catalysts to obtain a 3D network which is considered today as the state-of-the-art molecular catalysts for oxygen reduction.

According to the US-DOE, one of the most significant issues in fuel cells technology is their durability. In addition to their high activity, translated into high energy density, the materials themselves, mostly the catalyst, support and membrane, have to be stable and show durability over long periods of operation and under exposure to extreme conditions. In order to study the durability of fuel cells and their degradation mechanisms Lior's group is developing methodologies for accelerated stress tests (ASTs), based on the strength and weaknesses of the different materials used. These tests are designed to simulate the behavior of a fuel cell working over months and years in very short times (up to a week). So far they have developed tests for alkaline fuel cells together with GenCell, an Israeli startup company that currently relies on these test in the design of their products. In addition, the Elbaz group has developed test for ceramic materials and currently working on specific tests for non-precious metal catalysts. These studies enable them to pinpoint the weakest links in the cells and mitigate their durability issues via the design and engineering of new materials.

One good example for such materials are the ceramic supports developed in the Elbaz lab. Catalyst support durability is currently a technical barrier for polymer electrolyte membrane (PEM) fuel cells, especially for applications that demand high power. Degradation and corrosion of the conventional carbon supports lead to losses in active catalyst surface area and, consequently, reduced performance. As a result, the major aim of this project is to develop support materials, based on electronically conductive ceramics, that interact strongly with Pt, yet sustain bulk-like catalytic activities with very highly dispersed particles. Lior's group is developing next-generation platinum supported on molybdenum carbide, titanium carbide, titanium nitride and others. In their most recent publication, they showed more than 3X durability and higher activity with Pt/Mo_2C as compared to commercial Pt/C electrodes. In addition, they also work on carbon-based materials, mainly 2D materials such as graphene, and increase their tolerance to oxidative environment by doping them with nitrogen, sulfur and boron. The preliminary results are very promising, and these materials are already showing very good corrosion resistance.

Dan Major 's group

Current Team Members working

First Name	Last Name	Role
Amreen	Bano	Post-doc
Khorsed	Alam	Post-doc
Shira	Zilberzweig	PhD student (w/Noked)
Orly	Aminov	MSc student (w/Noked)

Research Topics:

1) Computational design of doped Ni-rich layered cathode oxide materials
2) Development of theoretical methods for electrode materials
3) Understanding of ALD coating mechanism
4) Developing machine learning models for battery failure

Ultimate Research Goals in the Framework of Inrep2:

1. Design of dopants for Ni-rich layered cathode oxide materials
2. Develop new general methods for use in energy research
3. Computational support for experimental groups

Relevant Instrumentation in your lab:

1. High performance computers

Major Achievements for FY2021:

1. Understanding and design of new dopants for Ni-rich layered cathode oxide materials
2. Development of new theoretical method for prediction of cation distribution in electrode materials
3. Construction of initial models for ALD processed
4. Initial ground work for developing machine learning models

Go/no-Go points:

1. n/a

Plans for FY 2022 (please relate to the US DOE bench marks and goals):

1. Complete mapping of dopants in Ni-rich layered cathode oxide materials
2. Study reactions related to atomic layer deposition
3. Build computer code and computational protocols for ALD coatings
4. Develop machine learning models for battery failure

Relevant Publications 2021:

1. Kim, B.; Kang, K. Expert Opinion: Major, D. T. Stabilizing oxygen redox chemistry for the realization of high-capacity batteries. *Nat. Sustain.* **2022**. https://doi.org/10.1038/s41893-022-00891-y.
2. Turgeman, M.; Wineman-Fisher, V.; Malchick, F.; Saha, A.; Bergman, G.; Gavriel, B.; Penki, T. R.; Nimkar, A.; Baranauskaite, V.; Aviv, H.; Fan, T.; Tischler, Y. R.; Levi, M. D.; Noked, M.; Major, D. T.; Shpigel, N.; Aurbach, D. **New Cost-effective Aqueous Electrolyte Enables Highly Stable Operation of 2.15V Lithium-Ion Battery.** ***Cell Reports Physical Science*** **2022, *3*, 100688.**
3. Shpigel, N.; Chakraborty, A.; Malchik, F.; Bergman, G.; Nimkar, A.; Gavriel, B.; Turgeman, M.; Hong, C.; Lukatskaya, M. R.; Levi, M.; Gogotsi, Y.; Major, D. T.; Aurbach, D. Can anions be inserted into MXene? *J. Am. Chem. Soc.* **2021**, 143, 12552-12559.
4. Susai, F. A.; Raman, R.; Chakraborty, A.; Leifer, N.; Nanda, R.; Kunnikuruvan, S.; Kravchuk, T.; Grinblat, J.; Ezersky, V.; Sun, R.; Deepak, F. L.; Erk, C.; Wu, X.; Maiti, S.; Sclar, H.; Goobes, G.; Major, D. T.; Talianker, M.; Markovsky, B.; Aurbach, D. Boron Doped Ni-Rich $LiNi_{0.85}Co_{0.10}Mn_{0.05}O_2$ Cathode Materials: Uniqueness of a Small-Size Dopant Studied by Structural

Analysis, Computational Modeling, Electrochemical Performance, and Monitoring ^{6}Li and ^{11}B in Cycled Electrodes. *Energy Storage Mater.* **2021**, 42, 594-607.

5. Levartovsky, Y.; Chakraborty, A.; Kunnikuruvan, S.; Maiti, S.; Grinblat, J.; Talianker, M.; Major, D. T.; Aurbach, D. Enhancement of structural, electrochemical, and thermal properties of high energy density Ni-rich $LiNi_{0.85}Co_{0.1}Mn_{0.05}O_2$ cathode material for Li-ion batteries by niobium doping. *ACS Appl. Mater. Interfaces* **2021**, 13, 34145-34156.
6. Levartovsky, Y.; Kunnikuruvan, S.; Chakraborty, A.; Maiti, S.; Grinblat, J.; Talianker, M.; Major, D. T.; Aurbach, D. Electrochemical and structural studies of $LiNi_{0.85}Co_{0.1}Mn_{0.05}O_2$, a cathode material for high energy density Li-ion batteries, stabilized by doping with small amounts of tungsten. *J. Electrochem. Soc.* **2021**, 168, 060552.

Presentations at Conferences 2019 - 2020:

1) n/a

Grants 2018:

2021-2023	Ministry of Energy (450,000 NIS) (w/Noked)
2020-2022	MAFAAT (400,000 NIS)
2019-2022	GIF (240,000 Euro)
2019-2022	Ministry of Science and Technology (1,500,000 NIS)
2018-2022	ISF (1,000,000 NIS)
2016-2021	INREP National Renewable Energy center member

Other activities:

n/a

Summary of work

1) Computational design of new Ni-rich Li-based layered Ni, Co, and Mn (NCMs) materials (w/Aurbach group). NCM-based materials are studied using classical and density functional theory (DFT) levels of theory. In particular we investigated the effect of different dopant atoms on the electronic structure,

phase stability, electrochemical behavior, surface stability, oxygen release in different Li-based Ni rich NCMs (e.g. 85% and 90% Ni-content materials). The following dopants are being studied:

Charge state	Dopants
3+	Al, Nd, Y
4+	Ti, Zr
5+	Nb, Ta
6+	Mo, W

2) Studying intercalation in anode materials (MXenes) (w/Aurbach).
3) Studying water-in-salt systems using MD simulations (w/Aurbach)
4) Developing new approaches for studying organic anodes (e.g., PTCDA) and their interaction with electrolytes and chaotropic and kosmotropic ions (w/Aurbach).
5) Study ALD coatings on LNO and LCO using DFT methods. Main point is studying chemical mechanism (w/Noked).
6) Developing computer code and protocols for modeling large scale ALD systems for MD simulations (w/Noked).
7) Developing machine learning models for battery failure (w/Noked).

David Zitoun's group

Current Team Members working on power sources projects (not only INREP)

First Name	Last Name
Thazee Veettil	Veenish
Saadi	Kobby
Melina	Zysler
Hardisty	Samuel
Anya	Muzikansky
Anagha	Usha Vijayakumar
Guy	Rahamim

Research Topic/s:
1) Bromine based redox-flow batteries.
2) Solid State Electrolytes
3) Catalyst development for fuel cells
4) Catalyst Development of electrolyzers

Ultimate Research Goals in the Framework of INREP
1) High round-trip efficiency sustainable redox-flow battery system
2) Single-atom stable catalysts with stable activity

Relevant Instrumentation in your lab:
1) Gloveboxes
2) Battery-cyclers
3) Reactors (Parr and Glass)
4) Wet chemistry under inert conditions

5) Echem scanner
6) RRDE systems

Major Achievements 2020-2021
1) Corrosion tolerant HBr redox-flow battery
2) Development of the state-of the-art low-PGM catalyst for ORR
3) Development of the state-of the-art non-PGM catalyst for HER/OER

Go/no-Go points:
1) n/a
2)

Plans for FY 2022 (please relate to the US DOE benchmarks and goals):

1) Increase the durability of HBr RFBs
2) Develop single-atom catalysts

Relevant Publications 2021:

1. Hydrogen-Bromine Redox-Flow Battery Cycling with Bromine Complexing Agent: the Membrane Challenge

Kobby Saadi, Michael Kuettinger, Peter Fischer*, David Zitoun* Energy Technology 2021, 9, 2000978

2. Pd/□-NiOOH as H2 Oxidation Catalyst: Synthesis, Structure and Operando X-Ray Absorption Spectroscopy

Maria Alesker, Istvan Bakos, Veronica Davies, Qingying Jia, Luba Burlaka, Valeria Yarmiayev, Anya Muzikansky, Anna Kitayev, Miles Page, Sanjeev Mukerjee, David Zitoun* *Catal. Science and Technology* 2021, 11, 1337-1344

3. Carbon supported Pt-Ni octahedral electrocatalysts as a model to monitor nickel corrosion and particle detachment

Melina Zysler, Tal Klingbell, Charles Amos, Paulo Ferreira, David Zitoun *Catal. Science and Technology* 2021, 11, 4793-4802

4. Silver Oxygen Reduction Electrocatalyst in Alkaline medium: Ageing and Protective Coating

Anna Kitayev, Melina Zysler, Samuel Hardisty, Miles Page, Ervin Tal-Gutelmacher, David Zitoun Energy Technology 2021, 9, 2100546
https://doi.org/10.1002/ente.202100546

5. Selective Catalysis for Electrocatalytic Hydrogen Oxidation and Evolution Reactions Via Carbon Nanotube Encapsulation and Oxide Nano-Layer Deposition

SS Hardisty, K Saadi, D Zitoun 2021 ECS Meeting Abstracts, 1863

6. Evaluation of Mg[B(HFIP)4]2-Based Electrolyte Solutions for Rechargeable Mg Batteries

Ben Dlugatch, Meera Mohankumar, Ran Attias, Balasubramoniam Murali Krishna, Yuval Elias, Yosef Gofer, David Zitoun, Doron Aurbach ACS Appl. Mater. Interfaces 2021, 13 (46), 54894-54905 https://pubs.acs.org/doi/abs/10.1021/acsami.1c13419

7. Selective Catalyst Surface Access through Atomic Layer Deposition
Samuel S Hardisty, Shira Frank, Melina Zysler, Reut Yemini, Anya Muzikansky, Malachi Noked, David Zitoun ACS Appl. Mater. Interfaces 2021, 13 (49), 58827-58837 https://pubs.acs.org/doi/abs/10.1021/acsami.1c20181

8. In Situ Measurement of Localized Current Distribution in H2-Br2 Redox Flow Batteries Brenda Berenice Martinez Cantu, Peter Fischer, David Zitoun, Jens Tübke, Karsten Pinkwart 2021, 14(16), 4945
https://www.mdpi.com/1996-1073/14/16/4945

Presentations at Conferences 2021:

Conference	*Place and Date*	*Title of lecture*
Israel Materials Engineering Conference (in person)	Jerusalem, 12/2021	Nano-catalysts for Hydrogen-Bromine Redox-Flow batteries
ACS meeting	Digital, 04/2021	Shape controlled Pt-Cu and Pt-Ni Electrocatalysts
ECS meeting	Digital, 05/2021	Selective Catalysis for HOR/HER Via Carbon Nanotube Encapsulation and Oxide Nano-Layer Deposition
EMRS meeting	Digital, 05/2021	Carbon Nanotube Catalysts for Hydrogen-Bromine Redox-Flow batteries

Grants:

Period	***Funding Agency***	***Title***	***Amount of funding/ overall***	***Coordinator/ Partners***
2020-2022	*Israel Innovation Authority*	*KAMIN: Plasmon sensing*	*$100,000/ $200,000*	*DZ/Prof. Adi Salomon*
2020-2021	Israel Chemicals Ltd (ICL)	Sponsored Research on bromine complexing agents	$70,000	DZ

2020-2025	BIRD foundation	Solid-state electrolyte batteries	$535,000 / $10,000,000	BIRAD BIU /TAU/ Material Zone/ 3DB / U Maryland / Forge Nano
2021-2025	BSF	Electromagnetic activation of catalysis	$253,000	DZ
2021-2023	Israel Ministry of Energy	The orange fuel	$150,000	DZ

Other activities:

Summary of work

Hydrogen-bromine redox-flow batteries (RFBs)

Hydrogen-bromine redox-flow batteries (RFBs) technology offers an economic storage solution and is considered promising as a sustainable electricity storage solution due to its fast kinetics, highly reversible reactions and low chemical costs. The main bottleneck of conventional RFBs is the corrosion due to the bromine species which results in the high cost of systems and the rapid fading of the hydrogen catalyst performance in the highly corrosive environment. Catalyst poisoning is a prominent issue, reducing the lifetime of catalysts and increasing the costs of the processes that rely on them. My group and collaborators (and Prof. Noked, BIU) have investigated the use of complexing agent to lower the concentration of free bromine (ref. 1, with Dr. Fischer, ICT Fraunhofer) and the use of segmented cells to monitor the local corrosion/activity (ref. 8, with Dr. Fischer, ICT Fraunhofer). We explored the oxide coating on catalysts (ref. 7, with Prof. Noked, INREP) and nanotube encapsulation (ref. 5)

Fuel cell catalysts

The oxygen reduction reaction (ORR) is a key process in Anion Exchange Membrane Fuel Cells (AEMFC). The alkaline conditions should allow silver (Ag)-based cost-efficient catalysts to replace platinum group metal (PGM) materials. However, Ag electrochemical stability or lack of stability in alkaline medium has still to be demonstrated. In ref. 4, we report a facile method for enhancing the chemical stability of Ag catalysts in an alkaline environment by depositing a protective polydopamine (PDA) coating, enhanced via crosslinking with polyethyleneimine (PEI), on the surface of Ag NPs.

The Hydrogen oxidation reaction (HOR) kinetics on pure precious group metals are very sluggish in alkaline medium. In ref.2, we report on an effective high-surface area carbon supported Pd/□-NiOOH HOR electrocatalyst from organometallic precursors. Contrary to previous reports where alloying phase could not be excluded, the novel phase and crystallographic orientation of the nickel oxo-hydroxide (□-NiOOH) pyramids (< 2 nm in size) have been fully ascribed through high resolution transmission electron microscopy, leaving no doubt about the nature of electrocatalytic surfaces.

Daniel Nessim's group

Current Team Members working on INREP related projects:

First Name	Last Name
Rajashree	Konar
Madina	Telkhozhayeva
Bibhudatta	Malik
Efrat	Shawat Avraham
Baruch	Hirsch
Sneha	Patil

Research Topic/s:

1. Development of nanostructured materials for Li-ion batteries
2. Development of nanostructured materials for fuel cells
3. Development of OER/HER catalysts

Relevant Instrumentation in your lab:

1. Two CVD systems under hood with multiple gas feeds
2. Potentiostat for basic electrocatalysis
3. Basic photocatalysis

Major Achievements for FY2018 (please relate to the US DOE bench marks and goals):

1. Development of 2D layered materials for Li-ion batteries (e.g., WSe2) and coatings
2. Development of many 2D layered materials for electrocatalysis

Go/no-Go points:

n/a

Plans for FY 2022:

1. Develop and test new nanostructured materials for batteries and fuel cells
2. Functionalize materials from other INREP groups

Relevant Publications 2021/22:

1. B. Malik, H. Sadhanala, R. Sun, F. Deepak, A. Gedanken*, and **G.D. Nessim*** *Co3O4/CoP Core-Shell Nanoparticles with Enhanced Electrocatalytic Water Oxidation Performance*

ACS Applied Nano Materials **[5.1]** (in press)

2. B. Malik, S. Majumder, R. Lorenzi, I. Perelshtein, M. Ejgenberg, A. Paleari, and **G.D. Nessim***
Promising Electrocatalytic Water and Methanol Oxidation Reaction Activity by Nickel Doped Hematite-Surface Oxidized Carbon Nanotubes Composite Structures
ChemPlusChem **[2.9]** 87, e2022000, May 2022

3. R. Konar and **G.D. Nessim***
A Mini-Review Focusing on Ambient-Pressure Chemical Vapor Deposition (AP-CVD) Based Synthesis of Layered Transition Metal Selenides for Energy Storage Applications
Materials Advances **[n/a]**, Vol. 3, 4471-4488, April 2022

4. M. Sadipan, R. Konar, H. Sclar, J, Grinblat, M. Talianker, M. Tkachev, X. Wu, A. Kondrakov, G.D. Nessim, and **D. Aurbach***
Stabilizing High-Voltage Lithium-Ion Battery Cathodes Using Functional Coatings of 2D Tungsten Diselenide
ACS Energy Letters **[23.1]** 7, 1383−1391, March 2022

5. B. Malik, H. Sadhanala, SKT Aziz, S. Majumder, R. Konar, A. Gedanken, and **G.D. Nessim***
Synergy between Cobalt Chromium Layered Double Hydroxide Nanosheets and Oxidized Carbon Nanotubes for Electrocatalytic Oxygen Evolution
ACS Applied Nano Materials **[5.1]**, 5, 3, 4091–4101, March 2022

6. A. Saha, N. Shpigel, N .Leifer, S. Taragin, T. Sharabani, H. Aviv, I. Perelshtein, **G.D. Nessim***, **M. Noked***, and Y. Gogotsi
Enhancing the Energy Storage Capabilities of Ti3C2Tx MXene Electrodes by Atomic Surface Reduction
Advanced Functional Materials **[18.8]**, Vol.31, issue 52, December 2021

7. B. Malik, **K.V. Sankar***, S.K.T. Aziz, S. Majumder, Y. Tsur, and **G.D. Nessim***
Uncovering the Change in Catalytic Activity during Electro-oxidation of Urea: Answering Overisolation of the Relaxation Phenomenon
Journal of Physical Chemistry C **[4.1]**, 125, 42, 23126–23132, October 2021

8. S.K.T. Aziz, S. Kumar, Sk Riyajuddin, **K. Gosh***, **G.D. Nessim***, and **D.P. Dubal***
Bimetallic phosphides for hybrid supercapacitors
The Journal of Physical Chemistry Letters **[6.5]**, 12, 21, 5138–5149, May 2021

9. B. Malik, K.V. Sankar, R. Konar, Y. Tsur, and **G.D. Nessim***
Determining the Electrochemical OER Kinetics of $Fe_3S_4@Ni_3S_2$ *Using Distribution Function of Relaxation Times*
ChemElectroChem **[4.6]**, 8, 517 – 523, Feb. 2021

10. R. Konar, S. Das, E. Teblum, A. Modak, I. Perelshtein, J.J. Richter, **A. Schechter***, and **G.D. Nessim***
Facile and Scalable Ambient Pressure Chemical Vapor Deposition-Assisted Synthesis of Layered Silver Selenide (β-Ag_2Se*) on Ag foil as an Oxygen Reduction Catalyst in Alkaline Medium*
Electrochimica Acta **[6.9]**, 370, 137709, Jan. 2021

Presentations at Conferences 2021/22:

1. *The Versatility of CVD to Synthesize 1D and 2D Nanostructures: Carbon Nanotubes and Transition Metal Chalcogenides for Electronic and Electrochemical Applications*
   International Conference on Contemporary Catalysis, Energy and Sustainability - 22 June 2022 online conference co-organized by Mahatma Gandhi University (MGU), in collaboration with Ben-Gurion University (BGU) of the Negev and Ariel University (AU), Ariel **(plenary)**

2. *The Versatility of CVD to Synthesize 2D Nanostructures: Carbon Nanotubes and Transition Metal Chalcogenides for Electronic and Electrochemical Applications*
   ISEL 2022 (Israel Electrochemical Society) at Ariel University, 26 May 2022 **(invited)**

3. *Spaghetti and lasagne: the cooking of 1D and 2D nanomaterials*
   IMEC 2021 in Jerusalem, 13-12-2021
   (My talk was delivered by Madina Telkhozhayeva since I was in covid quarantine)

4. *The Versatility of CVD to Synthesize 1D and 2D Nanostructures—Carbon Nanotubes and Transition Metal Chalcogenides for Electronic and Electrochemical Applications*
   Symposium: Advanced atomic layer deposition and chemical vapour deposition techniques and applications; 2D materials
   2021 MRS Fall Conference (Nov. 28th – Dec. 3rd, 2021) in Boston **(invited)**

5. *High Yield, Bottom-Up/Top-Down Synthesis of 2D Layered Metal Sulfides, Phosphides, and Selenides Using Chemical Vapor Deposition with applications in electronics and electrochemistry*
   NanoIL, Jerusalem, 4-6 October, 2021 **(invited)**

6. *Towards the Growth of 3D Forests of Carbon Nanotubes—Selective Height Control Using Thin-Film Reservoirs and Overlayers*
   63rd Electronic Materials Conference (EMC, organized by MRS), 23/6/2021, online

7. *High Yield, Bottom-Up/Top-Down Synthesis of 2D Layered Metal Sulfides, Phosphides, and Selenides Using Chemical Vapor Deposition with applications in electronics and electrochemistry*
   63rd Electronic Materials Conference (EMC, organized by MRS), 23/6/2021, online

8. *High Yield, Bottom-Up/Top-Down CVD Synthesis of 2D Layered Metal Selenides—A Promising Class of Materials for Applications in Electronics and Electrochemistry*
   MRS Spring Conference, session NM07.14: Devices for Sensing, Energy Conversion, and QIS II
   April 20, 2021, online **(invited)**

9. *Chemical vapor deposition synthesis of bulk layered metal chalcogenides (sulfides, phosphides, and selenides) in high yield and their applications in electrochemistry*

2DMAT2021, August 23-26, 2021, Paris, France – did not travel due to covid **(invited)**

10. *Spaghetti & Lasagne: the cooking of 1D and 2D nanomaterials*
    International Conference on Porous Materials for Energy and Environment
    12 March 2021, online **(keynote)**

Grants 2021/2022:
ISF in 2021
Kamin in 2022

Other activities:

2020-present: President of Israel Vacuum Society (IVS)

David Cahen's group

Current Team Members working on combinatorial research for finding new solid-state Li-ion conductors-related projects:

First Name	Last Name
Shay	Tirosh
Assistance has been provided by other group members.	

Research Topic/s:

1. Developing a high throughput characterization method for solid-state Li-ion conductors.
2. Apply high throughput combinatorial approach to find new solid-state Li-ion conductors.

Ultimate Research Goals in the Framework of the INREP:
New highly stable, highly conductive solid-state Li-ion conductor with negligible electron conduction properties.

Relevant Instrumentation in our labs or in BIU / BINA research services:

1. Combinatorial fabrication systems
   a. Sputtering,
   b. PLD, incl. (2021) novel bPLD*
   c. Multi-head Spray Pyrolysis*
2. High throughput characterization scanners (e.g., EDS, XRF, XRD, UV-Vis absorption*, PL)
3. Glove- and Dry*-boxes
4. FIB
5. XPS
6. Li-ion conductivity mapping (EIS*, FTO darkening*)
7. RBS.

**: home-built, or home-modified, often unique.*

Major Achievements for FY2021:

1. Multi-head spray pyrolysis as new tool for combinatorial synthesis in general has been accomplished. It was tested for oxides, sulfides and phosphides, and with focus on solid-state Li-ion conductors;
2. In a fabricate library of Li-La-P-O-based continuous composition spread we accomplished the lowest activation energy of conduction of 0.2eV for $Li_3La_3PO_x$, typical of inorganic ceramic electrolytes.
3. Max Li-ions conduction is of $1.4x10^{-9}$ S/cm. obtain for $LiLaP_{0.5}O_x$.

(We suppose that low Li-ion conductivity and low activation energy for Li migration discrepancies is due to sub-optimal occupation of lithium sites in the lithium lanthanum phosphate lattice. Instead, or in addition, issues of porosity and tortuosity may well limit Li-ion conductivity).

Go/no-Go points:

n/a

Plans for FY 2022:

The activity under INREP has been terminated.

Which components developed in your lab in recent years can be implemented in a Li-ion battery development today (also include a scale in size and weight when relevant):

Multi-head spray pyrolysis system as a high throughput, rational combinatorial approach for fabrication of material libraries in searching for new Li-ion conductors and, in general, for materials needed for INREP.

Relevant Publications 2021:

A. Usha Vijayakumar, N. Aloni, V. Thazhe Veettil, G. Rahamim, S. S. Hardisty,M. Zysler, S. Tirosh, and D. Zitoun*
Combinatorial Synthesis and Screening of a Ternary NiFeCoOX Library for the Oxygen Evolution Reaction
Submitted at 24-Nov-2021 and later published at *ACS Applied Energy Materials* **2022** *5* (4), 4017-4024.

Presentations at Conferences 2021:

n/a

Grants 2021:

MOE **תאים סולריים מבוססי פרבוסקיט הלידי מעורב עבור תאי טנדם עם סיליקון**

2019-2021: ש"ח 217000X3

SolarERA NET dry production routes for large area meatal halide perovskites

2020-2022 ש"ח 25000x3

ISF china – Israel •2D/3D composites to stabilize 3D halide perovskites of high optoelectronic quality

2020-2022 ש"ח 350000x3

BSF **Mitigating Losses at Halide Perovskite / Contact Interfaces**

2020-2023 $37500x4

This includes full coverage of all the work done by the TAU group of Golodnitsky in our labs for INREP, as the TAU group turned down our request to contribute.

Other activities:

Collaborative work with Prof. Zitoun (out of INREP farm). The Multi-head spray pyrolysis system as a high throughput, combinatorial approach has been used also by Prof. Zitoun (INREP member) for electro-catalysts and oxygen evolution reaction materials. It was including guiding consulting and assistance. Later at the end of 2021 the system has been delivered to Prof. Zitoun for further utilization.

Summary of work

In 2021 we were mainly focusing on continuing our work with the multi-head spray pyrolysis to use as high throughput combinatorial fabrication, for Li-ion conduction films.

We continued testing our hypothesis that in case solvents with similar rheological properties are co-sprayed under the same spraying conditions they will spray the same amount of material on a certain point in a library.

Analysis of the calibration data based on spraying dye from each nozzle, and the XRF of a model system containing Ni, La, and Cu, followed data obtained last year. Specifically, we attempted to realize the correlation between the composition indicated by the dye calibration and the XRF. Those attempts followed fitting and corrections. For example, we have tried to use correction parameters formed after fitting the compositions obtained from the calibrated to XRF data of a single row or single column in the middle of a library and to use those parameters to correct for the entire library.

In a separate test, we realized that the XRF is sample preparation dependent. Specifically, it is unreliable in case the sample is powdery or highly porose. We concluded that technically, we were unable to support our hypothesis.

At this stage of the research after similar failures to use also RBS (2020) for similar correlations we decided to stop this direction in research. Instead, we focused on determining the composition using ICP in selected cells (on the library) of interest where we measured interesting activation energy for ion migration and Li-ion conduction.

Each specific cell of interest was dissolved to determine its composition using ICP. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was done using a SPECTRO ARCOS ICP-OES Multi view FHX22 (Spectro Analytical, Kleve, Germany). Eleven 25 mm2-area samples, taken from different locations in the library, were dissolved in aqua regia (1:3 HNO_3:HCl volume ratio). A ten times diluted (by distilled water) solution was tested by ICP-OES for elemental analysis of Li, La, and P. A reference material, made by mixing 1:1:1 LiAc:LaAc: $(NH_4)_2HPO_4$ with subsequent 400°C heat treatment was also dissolved and analyzed by ICP-OES.

Malachi Noked's group

Dmitry Bravo	PhD, Senior researcher	Sri-Harsha Akla	PhD student
Ayan Mukhrejee	PhD, Senior researcher	Ananya Madegala	PhD student
Sivan Okashy	PhD, Senior researcher	Shalev Blanga	PhD student
Hagit Aviv	PhD, Lab Manager	Sarah Targin	PhD student
Arka Saha	Postdoc	Shira Frank	PhD Student
Sankalpita Chakrabarty	Postdoc	Orly Aminov	MSc Student
LongLong Wang	Postdoc	Rachelle Rosenberg	MSc student
Ortal Lidor-Shalev	Postdoc	Yakir Lampel	MSc student
Rosy Sharma	Postdoc (in part)	Tehila Mashita	MSc student
Eliran Evenstein	PhD student	Nicole Leifer	Postdoc
Reut Yemini	PhD student		
Talya Sharabani	PhD student		

Research Topic/s in INREP:

1) Development of surface protection films for electrodes
2) OEMS studies of gas evolution from batteries.
3) Metallic Anode reversibility in polysulfide solutions
4) Solid State Batteries

Relevant Instrumentation in Noked's lab:

1) ALD
2) Plasma enhanced ALD
3) Online electrochemical Mass spec – directly connected to batteries.
4) Glove boxes.
5) Ball milling
6) Thinky mixer
7) Battery cycling channels.
8) Dr. Blade

Major Achievements for FY2021:

1) Development of up-scalable state-of the-art surface modification processes for cathodes.
2) Quantifying the effect of polysulfides concentration on lithium anode reversibility at various current rates.
3) Doping and surface coatings of in house Synthesized cobalt free, Ni rich cathodes for lithium (LNO) sodium (NVPF, NVPBr) and Mg (V2O5) systems.

Go/no-Go points:

1) Li/S cells without anode protection or 100% prevention of polysulfide dissolution is a NO GO for EV application.
2) Li/O2 is no go for EV

Plans for FY 2022:

1) Solid state batteries with 500 cycles, anode free.
2) Synthesis of cathodes with no vanadium for sodium ion batteries.
3) Development of ALD processes of SE for high voltage
4) Evaluation of parasitic reaction of stainless still at high voltages
5) Development of cathodes for Zinc Air batteries
6) Stabilization of SiOx/Graphite anodes with capacity of 1000 mAh/g

The group of Malachi Noked made progress in the following areas during 2021:

1. We stabilized our LNO cathodes by doping (for liquid based electrolyte) and coatings (for both solid and liquid) and demonstrated high capacity cathodes (>240mAh/g)
2. We protected with surface film our V2O5 cathode, and cycled our cathodes in rechargeable magnesium battery
3. We demonstrated that we can stabilize $LiCoO_2$ – LCO cathodes charged to 4.55V, by developing unique MLD coating.
4. We stabilized lithium and Mn rich NCM, with capacity of >250mAh/g for more than 250 cycles using patented ALD process.
5. We demonstrated stabilization of high voltage $LiMn_{1.5}Ni_{0.5}O_4$ cathodes by surface treatments of TiO_2.
6. We developed new chemistries for ALD protection on electrochemically active materials.
7. We examined new electrolyte solutions and new red-ox polymer cathodes for rechargeable Mg batteries.
8. We started a new project aiming at developing nonaqueous Na ion batteries for large energy storge (together with Aurbach group, supported by the Israeli company Dor-Al).
9. We started working on recycling of NCM cathode materials.
10. We synthesized solid electrolytes for lithium ion with conductivity >2.5mS/cm
11. On the analytical side: we are making a further progress with OEMS based methodologies for evaluating gas evolution from various batteries.

Collaborations

During 2021 we maintained vital collaborations with the following industries:

1. Specific Polymers (France)
2. SAFT, Forge Nano and Ion storage (USA)
3. ICL (Israel)

4. We have academic collaborations with the groups of Eric Wachsman, Paul Albertus, Gary Rubloff and Ozgur Capraz (USA). Prof. Sagar Mitra (IIT Bombay), Prof. Xiulin Fan (China), and the emagic consortium (Horiszon 2020).
5. We are part of a new European Consortium E-Magic which includes the groups of Ein- Eli and Noked from Israel + groups from Spain, Germany, France, Denmark and the UK, developing rechargeable Mg batteries.
6. We have on-going collaboration through USA – Israel consortium supported by the BIRD foundation and the DOE - USA which explore solid electrolytes and develop solid-state batteries together with two INREP groups from BIU, two INREP groups from TAU, several Israeli and American start-up companies and research groups in the University of Maryland USA.

Within INREP we have collaborations now with Michal Leskes, Menny Shalom, David Zitoun, Doron Aurbach, Dan Major, Dina Golodnitsky, and Emanuel Peled.
Our work is very well documented in relevant papers during 2021.

Publications in 2021 (related to the INREP activities):

1. Maiti, S., Sclar, H., Sharma, R., Vishkin, N., Fayena-Greenstein, M., Grinblat, J., Talianker, M., Burstein, L., Solomatin, N., Tiurin, O., Ein-Eli, Y., Noked, M., Markovsky, B., Aurbach, D., Understanding the Role of Alumina (Al2O3), Pentalithium Aluminate (Li5AlO4), and Pentasodium Aluminate (Na5AlO4) Coatings on the Li and Mn-Rich NCM Cathode Material 0.33Li2MnO3·0.67Li(Ni0.4Co0.2Mn0.4)O2 for Enhanced Electrochemical Performance. Adv. Funct. Mater. 2021, 31, 2008083.

2. M. Noked, H. Ben-Yoav, E. Keinan, Rosarium Philosophorum on Electrochemistry, Isr. J. Chem. 2021, 61, 3.

3. Shira Haber, Rosy, Arka Saha, Olga Brontvein, Raanan Carmieli, Arava Zohar, Malachi Noked, and Michal Leskes Structure and Functionality of an Alkylated LixSiyOz Interphase for High-Energy Cathodes from DNP-ssNMR Spectroscopy, Journal of the American Chemical Society 2021 143 (12), 4694-4704

4. Reut Yemini and Malachi Noked, Effect of Polysulfide Species on Lithium Anode Cycle Life and Reversibility in Li–S Batteries, ACS Applied Energy Materials 2021 4 (5), 4711-4718

5. Reut Yemini, Shira Frank, Michal Natan, Gila Jacobi, Hagit Aviv, Melina Zysler, Ehud Banin, and Malachi Noked, Biofilm-Protected Catheters Nanolaminated by Multiple Atomic-Layer-Deposited Oxide Films, ACS Applied Nano Materials 2021 4 (6), 6398-6406

6. Poushali Das, Sayan Ganguly, Arka Saha, Malachi Noked, Shlomo Margel, and Aharon Gedanken, Carbon-Dots-Initiated Photopolymerization: An In Situ Synthetic Approach for MXene/Poly(norepinephrine)/Copper Hybrid and its Application for Mitigating Water Pollution, ACS Advanced materials and interfaces Articles ASAP

7. Wang, L., Sun, X., Ma, J., Chen, B., Li, C., Li, J., Chang, L., Yu, X., Chan, T.-S., Hu, Z., Noked, M., Cui, G., Bidirectionally Compatible Buffering Layer Enables Highly Stable and Conductive Interface for 4.5 V Sulfide-Based All-Solid-State Lithium Batteries. Adv. Energy Mater. 2021, 2100881.

8. Rosy, Sarah Taragin, Eliran Evenstein, Sebastian Maletti, Daria Mikhailova, and Malachi Noked, Diethylzinc-Assisted Atomic Surface Reduction to Stabilize Li and Mn-Rich NCM ACS Applied Materials & Interfaces 2021 13 (37), 44470-44478

9. Sri Harsha Akella et al and M.Noked* 2021 J. Electrochem. Soc. 168 080543

10. Shahar Dery, Hillel Mehlman, Lillian Hale, Mazal Carmiel-Kostan, Reut Yemini, Tzipora Ben-Tzvi, Malachi Noked, F. Dean Toste, and Elad Gross Site-Independent Hydrogenation Reactions on Oxide-Supported Au Nanoparticles Facilitated by Intraparticle Hydrogen Atom Diffusion ACS Catalysis 2021 11 (15), 9875-9884

11. Maddegalla, A., Mukherjee, A., Blázquez, J.A., Azaceta, E., Leonet, O., Mainar, A.R., Kovalevsky, A., Sharon, D., Martin, J.-F., Sotta, D., Ein-Eli, Y., Aurbach, D. and Noked, M. (2021), AZ31 Magnesium Alloy Foils as Thin Anodes for Rechargeable Magnesium Batteries. ChemSusChem. https://doi.org/10.1002/cssc.202101323

12. Sankalpita Chakrabarty et al and M. Noked* 2021 J. Electrochem. Soc. 168 080526

13. Lidor-Shalev, O., Leifer, N., Ejgenberg, M., Aviv, H., Perelshtein, I., Goobes, G., Noked, M. and Rosy, (2021), Molecular Layer Deposition of Alucone Thin Film on LiCoO2 to Enable High Voltage Operation. Batteries & Supercaps. https://doi.org/10.1002/batt.202100152

14. Saha, A., Shpigel, N., Rosy, , Leifer, N., Taragin, S., Sharabani, T., Aviv, H., Perelshtein, I., Nessim, G. D., Noked, M.*, Gogotsi, Y., Enhancing the Energy Storage Capabilities of Ti3C2Tx MXene Electrodes by Atomic Surface Reduction. Adv. Funct. Mater. 2021, 2106294. https://doi.org/10.1002/adfm.202106294

15. Sharabani, T., Taragin, S., Perelshtein, I., Noked, M., Mukherjee, A., Interfacial Engineering of $Na_3V_2(PO_4)_2F_3$ Hollow Spheres through Atomic Layer Deposition of TiO_2: Boosting Capacity and Mitigating Structural Instability. *Small* 2021, 17, 2104416.

16. Samuel S. Hardisty, Shira Frank, Melina Zysler, Reut Yemini, Anya Muzikansky, Malachi Noked, and David Zitoun *ACS Applied Materials & Interfaces* **2021** *13* (49), 58827-58837

17. Sri Harsha Akella, Sarah Taragin, Yang Wang, Hagit Aviv, Alexander C. Kozen, Melina Zysler, Longlong Wang, Daniel Sharon, Sang Bok Lee, and Malachi Noked *ACS Applied Materials & Interfaces* **2021** *13* (51), 61733-61741

List of grants:

Project Title	*Funding source*	*Amount*	*Period*	*Role*
European Magnesium Interactive Battery Community	Horizon 2020 Framework Program	6,731,937 € (for all participan-ts). 460,000 € to my lab.	2018-2022 48 months	co-PI
Lithium Oxygen study with OEMS	Binational Science Foundation	75,000 USD	2019-2021	PI
Surface protection of cathodes with ALD	KAMIN	660,000 NIS (330,000 to my lab)	2019 (with option for extension to 2 more years)	PI (Collaboration with Prof. Apeloig from Technion)
US-IL Energy center	BIRD foundation	20M USD for entire consortium (4M for BIU team)	2020-2024	Leading PI in Israeli Leading Institute (BIU)
ISF Individual Grant “Synthesis and utilization of Single Molecular Source for Molecular layer deposition of functional thin films as protective layer for lithium ion batteries cathodes”	ISF	1160000 NIS	2021-2025	PI
ISF-NSFC: Electrolyte and Interface Design for High-Safety and Wide-Temperature Lithium Secondary Batteries	ISF	870000 NIS	2021-2024	PI
EIC Transition	Horizon Europe	600000 Euro (for BIU)	2021-2023	Co-PI with collaborators from Czech republic and Germany

Work planned to 2022-2023:

We will continue to work on advanced cathodes for sodium, Mg and Li ion batteries.

We will continue to develop surface modifications for both anodes and cathodes.

New SiOx containing high specific capacity anodes (collaboration with Tadiran and 3DBatteries).

We will work intensively on developing Na ion batteries for large energy storage, in collaboration with Aurbach group at BIU, and the company Dor-Al.

Aurbach & Noked groups started working on rechargeable Zn-air batteries, in collaboration with Nichia , Japan. will continue to work on grafted high capacity activated carbon and carbonaceous red-ox active electrodes for aqueous sodium ion batteries

We will continue our on-going work on Mg batteries in collaboration with the groups of E-Magic consortium (an EC project), emphasizing solutions based on the solvent DME and the salt Mg-di [tetra (hexafluoro-isopropyl) borate] – $Mg[B(HFIP)_4]_2$. These solutions enables reversible Mg deposition in chlorides (Cl^-) free solutions. They may have high anodic and cathodic stability, enabling to develop high voltage/high energy rechargeable Mg batteries with magnesiated transition metal oxide cathodes (e.g. Mg_xVO_y compounds). There are a lot of aspects to explore, in order to ensure full reversibility (approaching 100%) of Mg metal anodes in them.

Adi Salomon's group

Cu Current group members:

First Name	Last Name
Ilya	Arad-Olevsko
Mohamed	Hemode
Alon	Krouse
Hodaya	Klimovsky
Tchyia	Zar
Omer	Shavit

Research Topic/s:

1) Fabrication of nanoporous 3D metallic electrodes and metallic nanostructures
2) 2-photon microscopy / SHG
3) Detection of near field phenomena by far-field optics
4) Nanoscopy
5) Hybrid photonic materials/ Strong coupling
6) Back focal plane imaging

7) Surface enhanced Raman spectroscopy, sensing
8) Axial metrology

Relevant Instrumentation in your lab:

1) 2-photon microscopy / SHG
2) Refractometry
3) Fluorescence microscopy, TIRF
4) Langmuir Blodgett

Relevant Publications 2021:

1. Sukharev, M., Salomon, A., & Zyss, J. **(2021)**. Second harmonic generation by strongly coupled exciton–plasmons: The role of polaritonic states in nonlinear dynamics. *The Journal of Chemical Physics*, 154(24), 244701.
2. Olevsko, I., Szederkenyi, K., Corridon, J., Au, A., Delhomme, B., Bastien, T., Fernandes, J., Yip, C., Oheim, M., & Salomon, A. **(2021)**. A simple, inexpensive and multi-scale 3-D fluorescent test sample for optical sectioning microscopies. *Microscopy Research and Technique*.
3. Salomon, A., Kollmann, H., Mascheck, M., Schmidt, S., Prior, Y., Lienau, C., & Silies, M. **(2021)**. Space- And time-resolved second harmonic spectroscopy of coupled plasmonic nanocavities. *Nanophotonics*.
4. Xue, X., Fan, Y., Segal, E., Wang, W., Yang, F., Wang, Y., Zhao, F., Fu, W., Ling, Y., Salomon, A., & Zhang, Z. **(2021)**. Periodical concentration of surface plasmon polaritons by wave interference in metallic film with nanocavity array. *Materials Today*, 46, 54–61.
5. Ron, R. and Salomon, A. Aerogel like metals produced through physical vapor deposition, ***Springer Nature*** *Handbook of Aerogels* **(2021).**

Presentations at Conferences 2021:

IMEC 2021	*Dec 2021* ***Invited*** *Jerusalem*	*Cathodoluminsence Nanoscopy of plasmonic structures*
Complex systems	*Oct 2021* ***Invited*** *Paris- Sacley*	*3D metallic networks*

Grants 2021:

Period	**Funding Agency**	**Title**
2021-2022	*Kamin (with Prof. David Zitoun)*	*משטחים מבוססי פלסמונים לשם זיהוי אופטי ברגישות גבוהה של מזהמים במים כגון מתכות כבדות, תרופות*
2020-2021	*Kamin*	*משטחים מבוססי פלסמונים לשם זיהוי אופטי ברגישות גבוהה של מזהמים במים כגון מתכות כבדות, תרופות*

2019-2022	*Eurostar (together with the Nano-center)*	***Nanoscale*** *- Nanopatterned Attachment for Nanometric Optical Standardization, Calibration and Length Estimation*
2019-2023	*ISF*	*Growth processes, optical characterization and interaction with molecules of large-scale nanoporous metallic networks*

Other activities:

- *Adi Salomon, Elad Segal and Adam Weissman Micron-Size plasmonic color sorter (2022) PCT/IL2017/050756, WO2018008029A1*
- *Martin Oheim and Adi Salomon. CALIBRATION STANDARD FOR EVANESCENCE MICROSCOPY PCT EP18306193.6. (2022)*

Summary of work

Many processes happen close to or at an interface. During the last 2 years we have developed far-field optical technique to retrieve information from the near field region. We can measure refractive index of thin films, thickness and emission pattern of fluorophores at the interface. In addition we have built axial nanometric ruler (metrology). In the next year we are going to develop in our lab Raman imaging technique for getting information only from surfaces/interfaces.

Ilya Grinberg's group

on INREP related projects (not only in the framework of the IFCC):

First Name	Last Name
Samala Nagaprasad	Reddy
Denial	Aias
Hodaya	Bochko
Atanu	Samantha
Ignacio Jose	Borge Duran

Research Topic/s:

1) Relationship between structure and activity of molecular ORR catalysts
2) Development of descriptors for durability of PGM-free catalysts
3) Investigation of the role of carbons in hydrazine oxidation

Ultimate Research Goals in the Framework of the IFCC:

1) Highly active ORR PGM-free catalysts for PEMFCs and AFC
2) Highly durable ORR PGM-free catalysts for PEMFCs and AFC

Relevant Instrumentation in your lab:

1) Linux High-performance Computing Cluster

Major Achievements for FY2021 (please relate to the US DOE bench marks and goals):

1) Revealed the origin of the rare high activity of Mn-based pyrolyzed catalysts
2) Developed a model for the arrangement energetics and phase transitions of Mo_2C and Ti_2C non-stoichiometric carbide
3) Showed that undoped carbon contributes to HzOR catalysis

Go/no-Go points:

n/a

Plans for FY 2022 (please relate to the US DOE bench marks and goals):

1) Identify degradation mechanisms for PGM-free catalysts in alkaline environment
2) Identify a quantitative descriptor of PGM-free catalyst durability
3) Design PGM-free catalysts resistant to protonation to obtain 10x or higher increased durability in acidic environment

Relevant Publications Relevant to INREP 2021:

1. V. K. Harika, T. R. Penki, B. Loukya, A. Samanta, G. L. Xu, C. J. Sun, **I. Grinberg,** F. L. Deepak, K. Amine, D. Aurbach*, and A. Gedanken*, "Sustainable existence of solid mercury (Hg) nanoparticles at room temperature and their applications". *Chemical Science*, *12*(9), 3226-3238 (2021).
2. A. Friedman, S. N. Reddy, H. C. Honig, M. Tasior, D.T. Gryko*, L. Elbaz*, **I. Grinberg***, "Control of Molecular Catalysts for Oxygen Reduction by Variation of pH and Functional Groups", *ChemSusChem* **4**, 1886-1892 (2021).
3. I. B. Duran, D. Aias and **I. Grinberg***, "Modeling of order-disorder transitions in non-stoichiometric carbides using a simple interatomic potential", *Physical Chemistry Chemical Physics* **23** (39), 22305-22312 (2021).
4. T. Y. Burshtein, D. Aias, J. Wang; M. Sananis, E. M. Farber, O. M. Gazit, I**. Grinberg**, and D. Eisenberg*," Fe–N–C Electrocatalysts in the Oxygen and Nitrogen Cycles: The Role of Iron Carbide", *Physical Chemistry Chemical Physics* **23** (47), 26674-26679 (2021).
5. S. Hardisty, K. Saadi, S. N. Reddy, **I. Grinberg** and D. Zitoun*, "Ionically Selective Carbon Nanotubes for Hydrogen Electrocatalysis in a Poisoning Environment", *Materials Today Energy* **24**, 100937 1-10 (2021).
6. T. Y. Burshtein, K.Tamakuwala, M.Sananis, **I.Grinberg**, N. R. Samala, D. Eisenberg," Understanding hydrazine oxidation electrocatalysis on undoped carbon", *Phys. Chem. Chem. Phys*., 2022, **24,** 9897-9903
7. S. N. Reddy and **I. Grinberg**, "Origin of the Rare High Performance of MnN 4 -doped Carbon ORR Catalysts", *ChemSusChem* (in press).

Grants 2021:

2018-2021: Computational studies and design of piezoelectric oxides ($230K; Funding Agency: Israeli Science Foundation (**ISF**)). PI: Ilya Grinberg

2019-2022: Compact monolithic wavelength-tunable microcavity diode laser based on electro-optic modulation of 2D nanomaterial thin films ($128K; Funding: Israeli Ministry of Science (**MoS**)). PI: G. Daniel Nessim, co-PIs: Yaakov Tischler, Ilya Grinberg.

Summary of work

To enable widespread use of fuel cells, it is necessary to reduce the cost of the fuel cell catalyst and increase its durability. Currently use Pt catalysts are too expensive for large-scale mass production. Their durability also needs to be improved. The high cost of Pt has motivated a worldwide effort to find platinum-group-metal free (PGM-free) catalysts. Most of these are metal doped carbon-nitrogen materials. Unfortunately, while these reduce the cost and have reached close to the performance of Pt, their durability is much lower. Further development of PGM-free catalysts is hampered by the lack of control of their active sites composition during synthesis.

Using first-principles calculations, we have studied the effects of the changes in the macrocycle structure, axial ligand, distance between active sites, interactions with dopant N atoms and the presence of an extended carbon network on the ORR catalysis of various Mn-, Fe-, and Co-based systems by comparing the adsorption energies of the ORR intermediates. We find that the sensitivity to the local environment changes is largest for Mn and smallest for Co, with Fe in the middle for systems. Our results showed that the strong binding of OH by Mn together with the strong sensitivity of the Mn to the modification of its environment necessitates a precise combination of local environment changes that are possible in pyrolyzed materials to achieve a high V_{onset} in Mn-based catalysts. By contrast, the weaker binding of OH by Fe and Co and their weaker sensitivity to local environment changes lead to a wide variety of local environments with favorable catalytic activity (V_{onset} >0.7 V) for Co- and Fe-based systems. This explains the scarcity of reported Mn-based pyrolyzed catalysts and suggests that precise material synthesis and engineering of the active site can achieve high-performance Mn-based ORR electrocatalysts with high activity and durability.

In collaboration with the group of David Zitoun, we have investigated the protective effect of carbon nanotubes for Pt catalysts inside the nanotubes for Br flow batteris. We found that the negatively charged Br is repelled by the nanotube whereas hydrogen can access the Pt catalysts inside the nanotube. This explains the higher stability of the encapsulated Pt catalysts observed experimentally.

To understand the degradation of the catalyst and the possible ways to improve the durability, we correlated the experimental corrole activity degradation with the electron-withdrawing nature of the substituent group and the likelihood of protonation. Our results suggest that decreasing protonation (obtaining lower pKa) strongly hinders the demetallation of the corrole catalysts, making it more stable. This for the first time provides guidance for rationaly designing more durable PGM-free catalysts.

In collaboration with the group of David Eisenberg, we have studied the activity of undoped carbon for hydrazine oxidation and showed that edge and other defect sites have some catalytic effect for hydrazine oxidation, and account for the large peak observed at high applied potential in hydrazine oxidation experiments.

In another project in collaboration with the experimental groups at LANOTEC (Costa Rica) for the study of lysine used as the binder in electrodes in Li-ion batteries, we have used computational modeling to suggest show that lysine is superior to the standard PVDF binder due to its higher conductivity.

We have also parameterized a simple model of interatomic arrangement in non-stoichiometric carbides that allowed us to accurately predict the transition temperatures and metal arrangement energetics in Mo_2C and Ti_2C carbides.

Tel – Aviv University

Emanuel Peled' group

Current Team Members working on Batteries and FC related projects (not only in the framework of the INREP):

	First Name	Last Name	Academic degree	Joint staff members and students with Prof. Golodnitsky
1	Yonatan	Horowitz	P.D.	v
2	Meital	Goor	Dr, researcher, lab manager	v
3	Gilat	Ardel	Dr, researcher	v
4	Lina	Faktorovich	Dr, researcher	
5	Yosi	Kamir	Technician	v
6	Dan	Schneier	PhD student	
7	Tzach	Mukra	PhD student	
8	Ido	Ben Barak	PhD student	v
9	Edi	Mados	MSc student	v
10	Chen	Ulavski	MSc student	
11	Assa	Tamir	MSc student	
12	David	Stark	Undergrad. Student, technician	v

Research Topic/s:

1) ORR catalysts development and characterization for PEM FCs and DMFCs;
2) Degradation of DMFC catalysts
3) Lithium sulfur batteries
4) Nano structure silicon anodes for EV lithium batteries
5) LMB - study the plating –dissolution process of lithium
6) 3D printing of lithium batteries
7) In operando study of Si lithiation by THz spectroscopy with Dr. Sharly Fleischer

Ultimate Research Goals in the Framework of the INREP:

1) Low Pt, durable and highly active core-shell ORR catalysts for PEM FCs
2) Fundamental understanding of the degradation of DMFC catalysts
3) Cooperation with Prof. Amir Nathan in order to determine the structure of 0.15 to 4ML of Ru on Pt and Pt on Ir.
4) High energy, high power, high coulombic efficiency (over 98 at the short range and over 99.8% at the long range) durable lithium sulfur battery
5) Development of LMB and anode free lithium metal batteries (AFLMB), with high lithium plating/dissolution current efficiency (over 99 at the short range and over 99.9% at the long range) and a shorts free process.

Relevant Instrumentation in your lab:

1) Three RRDE systems
2) BET
3) FC test station
4) Hot press for MEA fabrication
5) Five battery cyclers (over 200 channels)
6) Four glove boxes
7) Three Potentiostats + EIS system
8) Two EIS systems.
9) Two High-energy ball mill PM 200 (RETSCH).
10) A 3D ink – jet printer for lithium batteries.

Major Achievements for FY2021:

1. A quantitative study of 0.15 to 4ML of ruthenium on Pt, effects on surface structure (with Prof. Amir Nathan) and on ORR catalysts activity and durability
2. Understanding the ruthenium-contamination effect on Pt ORR catalysts in PEMFC and DMFC (with Prof. Amir Nathan).
3. Synthesis and characterization of Core-Multi –Shell ORR catalysts for PEMFCs.
4. Understanding the capacity losses processes in plating – dissolution of lithium in carbonate and ether based solutions.

5. Development of inks and procedures for printing of cathodes, anodes and separators by Drop-on-Demand system
6. Cycling behavior of Si based electrodes in Si/Li cells
7. Increasing the cycle life of AFLMB and LMB by four and two times respectively and enhancing the performance of Si and graphite anodes by addition of ceramic nanoparticles to the electrolytes:
8. Evaluating the passivating layer on freshly cleaved silicon

Plans for FY 2022 (please relate to the US DOE bench marks and goals):

1) Continue in-situ/Ex-situ PtRu anode GDEs degradation tests using XRD in order to fundamentally understand the dissolution of Ru from the anode.
2) Synthesis and characterization of Core-Multi–Shell catalysts for hydrogen evolution (HER) in electrolyzers (with prof. G. Markovich).
3) Continue to study the effect of several parameters on the losses in the lithium deposition– dissolution process in liquid electrolyte and in the SE/CC interphase.
4) Continue to study the effect of several parameters on the behavior of lithium – sulfur battery (with an Indian group, Prof. Manuel Stephan).
5) Studying the effect of ceramic nanoparticles on the behavior of Si nano structure anode, graphite anode and lithium metal anode.
6) Development and characterization of high power multi levels lithium batteries made by 3D drop on demand system (With RAFAEL).

Which components developed in your lab in recent years can be implemented in a battery and fuel cell today (also include scale in size and weight when relevant):

1) More active, lower Pt content and durable ORR core-shell catalysts.
2) Cathodes, separator and anodes made by 3D drop on demand printing system.
3) Durable lithium cells with SiNWs and SINPs anodes (a startup company, SILIB, was established.
4) Improving the cycle life of Si, graphite and LMB by addition of low concentrations of ceramic nano particles to the electrolyte (patent pending)

Relevant Publications 2021:

1. Y. Horowitz, E. Strauss, E. Peled and D. Golodnitsky, How to Pack a Punch – Why 3D Batteries are Essential? Israel Journal of Chemistry (accepted 12-2 - 2021)
2. E. Mados, N.Harpak, G. Levi , F. Patolsky, E. Peled and D. Golodnitsky;. Enhancing the Electrochemical Performance of Silicon-Nanowire Anodes; RSC Advances, 2021, 11, 26586–26593
3. D. Krotkov, D. Schneier, S. Menkin[2], Y. Horowitz[3], E. Peled, D. Golodnitsky and S. Fleischer; *In-operando* Terahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes , in revision ‘Batteries & Supercaps 7-2021

4. D. Schneier, N. Harpak[1], F. Patolsky, D. Golodnitsky, Emanuel Peled; Pouch-cell Architecture Downscaled to Coin Cells for Electrochemical Characterization of Bilateral Electrodes ; **Batteries&Supercaps accepted 20-1-2021.**
5. Schneier, Dan; Horowitz, Yonatan; Kasnatscheew, Johannes; Gruenebaum, Mariano; Wiemhöfer, Hans-Dieter; Winter, Martin; Peled, Emmanuel; Evaluating the Passivation Layer of Freshly Cleaved Silicon Surfaces by Binary Silane- based Electrolytes: Batteries & Supercaps (2021) 4, 1-10**.**
6. Tzach Mukra, Roy Marrache, Pini Shekhter and Emanuel Peled; Enhancing Performance of Anode-Free Li-metal batteries by Addition of Ceramic Nanoparticles, PART I , JES , in print 9 (2021)
7. Ido Ben-Barak, Dan Schneier, Yosef Kamir, Meital Goor, Diana Golodnitsky* and Emanuel Peled; Drop-on-Demand 3D-Printed Silicon-Based Anodes for Lithium-Ion Batteries Journal of Solid State Electrochemistry; JSEL accepted 10-(2021)

Presentations at Conferences 2021

N/A

Grants 2021:

2018-2021: Printed batteries ($500K; Funding: Israeli Ministry of Defence (MoD)). PIs: E. Peled, D. Golodnitsky

2018-2021: Direct Methanol Fuel Cell (DMFC) - Study of Catalysts Degradation Processes
(840,000 NIS PASI) P.I. E. Peled and D. Kaplan

2018-2021 INREP research grant

2018-2021 INREP infrastructure grant

2020 - 2022 Indian-Israel joint research cooperation with Prof. Manuel Stephan, 388000 NIS

2020 - 2022 Israeli-Italian scientific and technology cooperation with Prof. Piercarlo Mustarelli 350000 NIS

2020 – 2024 Israel – USA collaboration on solid state batteries. Consortium with groups at BIU, Maryland university USA, Israeli and American start-up companies, supported by BIRD foundation and the DOE USA.

Other activities:

2016-present: Volunteer advisor to the Israeli Navy regarding fuel cells

2019-present: Volunteer advisor to the Israeli Air Force regarding high energy lithium batteries

Summary of work

Enhancing Performance of Anode-Free Li-metal Batteries by Addition of Ceramic Nanoparticles

Because of their higher energy density, compared to lithium-ion batteries, rechargeable lithium-metal batteries (LMB) have been considered one of the most attractive next-generation energy-storage systems (ESS). A promising approach to improving LMB performance, that has gained interest in recent years, is the use of anode-free lithium-metal batteries (AFLMB). Such battery configuration enables elimination of the problem of using excessive amounts of lithium in LMBs, hence increasing the specific energy of the battery. Another approach is to use a solid-state electrolyte (SSE) which increases energy density and decreases safety concerns.

This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of AFLMB. It was found that the addition to the electrolyte of low concentrations of MONPs significantly improves coulombic efficiency (CE), capacity retention (CR) and the SEI properties. Cells with 1% In_2O_3 or 1% ZnO addition resulted in 99.6% and 99.5% CE, and CR of 70% within 46 and 39 cycles, respectively. Combination of these MONPs resulted in 99.9% CE.

Study of Ruthenium-Contamination Effect on Oxygen Reduction Activity of Platinum-Based PEMFC and DMFC Cathode Catalyst

We outline a systematic experimental and theoretical study on the influence of ruthenium contamination on the oxygen reduction activity (ORR) of a Pt/C catalyst at potentials relevant to a polymer electrolyte fuel cell cathode. A commercial Pt/C catalyst was contaminated by different amounts of ruthenium, equivalent to 0.15–4 monolayers. The resulting ruthenium-contaminated Pt/C powders were characterized by energy–dispersive x–ray spectroscopy (EDS), x–ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM) to verify ruthenium contamination. A rotating disk electrode (RDE) technique
was used to study the influence of ruthenium on oxygen reduction kinetics. Density functional theory (DFT) calculations were performed to estimate the oxygen reduction activity of the platinum surface with increasing ruthenium coverage, simulating ruthenium-contaminated Pt/C. The binding energies of O and OH on the surfaces were used for activity estimations. It was found that the specific activity of the ORR at 0.85 V vs RHE exhibited an exponential-like decay with increased ruthenium contamination, decreasing by ∼45% already at 0.15 monolayer-equivalent contamination. The results of the DFT calculationswere qualitatively in line with

experimental findings, verifying the ability of the chosen approach to predict the effect of ruthenium contamination on ORR on platinum.

Cycling behavior of silicon – based electrodes in Si/Li cells

Si/Li cells are very common in the study of silicon-type Li-ion anodes. When used with carbonate based liquid electrolytes, a common phenomenon of sudden capacity increase in the beginning of cell cycle life occurs. We use dQ/dV analysis to show that this phenomenon stems from reaction of partially lithiated amorphous silicon phases that are exposed to potential low enough to become fully lithiated. XRD analysis shows that this reaction forms amorphous rather than crystalline $Li_{3.75}Si$ phase. We use 3-electrode cells and accepted models for lithium-metal behavior to propose a model for the cause of this capacity increase – reduced availability for cyclable lithium ions causes pitting of the lithium metal, sharply decreasing its overpotential and allowing the lithiation of the silicon electrode to proceed. We show that modification to cycling parameters themselves, by changing the cycling voltage window or using constant-current-constant-voltage cycling, does not artificially form or prevents this phenomenon, as it is directly related to surface behavior of the lithium electrode. Other methods of mitigation, by using a different counter electrode or by 3-electrode cycling, are proposed.

Synthesis and electrochemical performance of silicon-nanowire alloy anodes

High-capacity materials are required in order to address the environmental concerns of our modern society, ultimately leading to safe and eco-friendly high-energy batteries. Silicon-nanowire anodes (SiNWs) have the potential to significantly increase the energy density of lithium-ion batteries (LIBs). In order to improve the mechanical durability and the electrochemical performance of SiNW-anodes, we fabricated a silicon–nickel (SiNi) composite anode by electroless deposition of nickel, followed by annealing at high temperature to obtain nickel silicides of different content and composition. The morphology of SiNi-alloy anodes was examined by SEM, in situ TEM and EDS methods in order to understand how different deposition protocols affect the coating of the silicon nanowires. The formation of Ni-silicides was found to occur during thermal treatment at 900 _C. Despite the incomplete shell coverage of SiNWs composed of multiple phases and grains, the electrochemical performance of
binder-free and conducting-additive-free SiNi-alloy anodes showed stable electrochemical behavior and higher capacity retention compared to the pristine SiNW anode. Li/SiNW–SiNix cells ran at C/2 rate for 200 reversible cycles, exhibiting 0.1%/cycle capacity loss after completion of the SEI formation.

Evaluating the Passivation Layer of Freshly Cleaved Silicon Surfaces by Binary Silane-Based Electrolytes

The expansion of silicon anodes in lithium-ion batteries during lithiation and the resulting instability of its solid-electrolyte interphase (SEI) has been its Achilles heel for quite some time.
Beyond the mechanical damage, this expansion exposes fresh elemental silicon to the electrolyte solution. The electrolytereadily decomposes on the reactive silicon surface. Researchers
that test novel electrolytes find it difficult to separate which of the electrolyte components (solvent or anion) decomposes first and diagnose the respective decomposition products. Here, we utilize a straightforward test protocol that reveals which reduces first on bare silicon. We exposed four electrolyte mixtures to elemental silicon in custom made T-cells by breaking thin silicon wafers in solution. We analyze the resulting surface film layers and compare their composition to the electrolyte's performance in symmetrical lithium cells, and Si/Li cells. We found that unstable anions rather than reactive solvents lead to poor electrochemical performance.

Drop-on-Demand 3d-Printed Silicon-Based Anodes for Lithium-Ion Batteries

We present the application of Drop-on-Demand dispensing technology for the printing of silicon-based anodes. We show that the DoD printing technique is highly suitable for the printing of arbitrary-geometry, high-activity SiNi nanoparticle anodes for Li-ion batteries. These anodes are on par with traditionally prepared anodes in terms of electrochemical behavior and performance and can be easily used in printed or any other type of Li-ion cells. We found that improved adhesion is necessary because of the complex geometry of printed anodes. High adhesion was achieved with the use of two types of CNT coatings on the copper current collector, and etching of the copper itself without the use of an intermediate coating. Printed anodes are electrochemically stable and perform according to most criteria as well as previously presented cast anodes, exhibiting high capacity (500—1200 mAh/g anode, depending on the type of cell) and have a relatively long cycle life (up to 500 cycles). Our results highlight novel strategies for 3D electrode printing for potential uses in specialized batteries and is of particular importance for advanced research and development. Printed electrodes shown here can be directly implemented as described, or be used as reference for the development of new types of electrodes for energy storage devices.

In-operando Terahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes

The *in-situ* characterization of materials and interphases of battery electrodes is of crucial importance for the basic understanding of the complex, simultaneous processes that take place during the operation of secondary batteries. Here we present, for the first time, the use of a Terahertz (THz) time-domain-spectroscopy method for the *in-operando* characterization of the silicon/electrolyte interfacial phenomena and dynamics in a working lithium-ion battery. Strong correlation between the THz, XPS, and electrochemical data was established, allowing us to monitor the formation and evolution of the solid electrolyte interphase (SEI) during the reversible lithiation of the silicon anode.

Diana Golodnitsky's group

Current Team Members working on Batteries and FC related projects (not only in the framework of the INREP):

	First Name	Last Name	Academic degree	Joint staff members and students with Prof. Peled
1	Yonatan	Horowitz	Dr, Postdoc student	v
2	Meital	Goor	Dr, researcher	v
3	Gilat	Ardel	Dr, researcher, lab manager	v
4	Yosi	Kamir	Technician	v
5	Ido	Ben Barak	PhD student	v
6	Heftsi	Ragones	Dr, Postdoc student	
7	Mikhail	Sivak	Dr, Postdoc student	
8	Edi	Mados	PhD student	
9	Moran	Livshitz	PhD student	
10	Inbar	Anconina	MSc student	
11	Adi	Vinograd	MSc student	
12	David	Stark	MSc student	
13	Keren	Mizrachi	Materials Science Project student	
14	Moty Marcus	Dorfman	Technician	

Research Topic/s:

1) 3D Silicon/Metal-Silicide Anodes for Lithium-Ion BatteriesProtective Layers on High-Voltage Cathodes
2) Study of ion transport in Solid Polymer-in-Ceramic Electrolytes
3) Nano structure silicon alloy anodes for EV lithium batteries
4) AC/DC electrophoretic deposition of solid electrolytes
5) Free Form-Factor Multi-Coaxial Cable Batteries
6) Development of ultra-thin battery by electrophotography method (in collaboration with HP)
7) In operando study of Si lithiation by THz spectroscopy with Dr. Sharly Fleischer

Ultimate Research Goals in the Framework of the INREP:

1) Fundamental understanding of the polymer/ceramic interfacial phenomena in composite solid electrolytes
2) High energy, high Coulombic efficiency (over 98 at the short range and over 99.8% at the long range) stable SiNW anodes
3) Development of protected NMC cathode, which exhibits high stability at above 4.4V.
4) Solvent-free preparation of flexible electrolyte

Relevant Instrumentation in your lab:

1) Three RRDE systems
2) BET
3) FC test station
4) Hot press for MEA fabrication
5) Five battery cyclers (over 200 channels)
6) Four glove boxes
7) Three Potentiostats + EIS system
8) Two EIS systems.
9) Two High-energy ball mill PM 200 (RETSCH).
10) A 3D ink – jet printer for lithium batteries.
11) Fused-deposition 3D printer (Up-Plus 2)
12) 4-head 3d printer (Micron)
13) Two filament extruders (Noztek Pro)
14) Home-made plain extruder for processing of small amounts of materials

Major Achievements for 2021:

1. Development of plasticized LiTFSI PLA-PEO electrolyte with bulk ionic conductivity of 1-4mS/cm at 60°C.
2. Development of in-operando THz spectroscopy method for batteries studies
3. Development of square-wave AC EPD of LTO-based anodes

Plans for FY 2022 (please relate to the US DOE bench marks and goals):

1) Continue development of solvent-free methods for the preparation of flexible solid electrolytes and electrodes.
2) In-depth studies of the mechanism of AC EPD
3) Mechanochemical synthesis of core/shell ion- and mixed-conduction electrolyte and electrode active materials.
4) Studying the effect of salt-superionic conductor interactions by DFT (with Amir Natan).
5) Development and characterization of high-power multi levels lithium batteries made by 3D drop on demand system (With Prof. Peled and RAFAEL).

Which components developed in your lab in recent years can be implemented in a battery and fuel cell today (also include scale in size and weight when relevant):

1) Membrane-electrode assembly for the thin-film batteries.
2) Cathodes, separator and anodes made by solvent-free methods.
3) Durable lithium cells with SiNWs and SINPs anodes (a startup company, SILIB, was established (together with Prof. Peled).
4) 3D Silicon/Metal-Silicide Anodes for Lithium-Ion Batteries

Relevant Publications 2021:

1. Yonatan Horowitz, Ela Strauss, Emanuel Peled and Diana Golodnitsky How to Pack a Punch - Why 3D Batteries Are Essential, invited paper, *Israel Journal of Chemistry*, 2021, 51, 38-50, https://doi.org/10.1002/ijch.202100001
2. Dan Schneier , Nimrod Harpak , Fernando Patolsky, Diana Golodnitsky. Emanuel Peled. Pouch-Cell Architecture Downscaled to Coin Cells for Electrochemical Characterization of Bilateral Electrodes *Batteries & Supercaps*, 2021, 4, 767 –770, https://doi.org/10.1002/batt.202000325
3. Edna Mados, Nimrod Harpak, George Levi , Fernando Patolsky, Emanuel Peled and Diana Golodnitsky, Synthesis and Electrochemical Performance of Silicon-Nanowires Alloyed Anode, *RSC Adv.*, 2021, 11, 26586, DOI: 10.1039/d1ra04703e
4. Krotkov, Daniel; Schneier, Dan; Menkin, Svetlana; Horowitz, Yonatan; Peled, Emanuel; Golodnitsky, Diana; Fleischer, Sharly OperandoTerahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes, invited paper, *Batteries & Supercaps*, 2021, 09, https://doi.org/10.1002/batt.202100183
5. Gayathri Peta, Shaul Bublil, Hadas Alon-Yehezkel , Ortal Breuer, Yuval Elias, Nethanel Shpigel, Miryam Fayena-Greenstein, Diana Golodnitsky and Doron Aurbach High-performance Na- Na3Ti2(PO4)3 battery systems with solid electrolytes based on PEO:$NaPF_6$, *J. Electrochem. Soc*. 2021, *11 https://doi.org/10.1149/1945-7111/ac330d*
6. Adi Vinegrad, Heftsi Ragones, Nishani Jayakody, Gilat Ardel, Meital Goor, Yossi Kamir, Moty Marcos Dorfman, Alexander Gladkikh, Larisa Burstein, Yonatan Horowitz, Steve Greenbaum and Diana Golodnitsky Plasticized 3D-Printed Polymer Electrolytes for Lithium-ion Batteries, , *J. Electrochem. Soc., 2021 168 110549*
7. Ido Ben-Barak, Dan Schneier, Yosef Kamir, Meital Goor, Diana Golodnitsky Emanuel Peled Drop-on-Demand 3D-Printed Silicon-Based Anodes for Lithium-Ion Batteries, *Journal of Solid State Electrochemistry*, 2021, 10 https://doi.org/10.1007/s10008-021-05056-z
8. Ido Ben-Barak, Heftsi Ragones and Diana Golodnitsky. 3D Printable Solid and Quasi-Solid Electrolytes for Advanced Batteries, invited paper, Electrochemical Science Advances journal, 2021, https://doi.org/10.1002/elsa.202100167

Presentations at Conferences 2021

Israel Electrochemical Society meeting, June 2021; CUNY, US, November 2021, virtual

Grants 2021:

2018-2021: Printed batteries ($500K; Funding: Israeli Ministry of Defence (MoD). PIs: E. Peled, D. Golodnitsky

2017-2021: High-Energy, Safe, Lithium Metal-Free Sulfur/Silicon Battery (300,000 Euro, GIBS) PI: D. Golodnitsky, M. Wohlfahrt-Mehrens, ZSW

2019-2021: Integrated 2D&3D Functional Printing of Batteries with Metamaterials and Antennas, 1,420,000 NIS. PIs: Y. Shacham, D. Golodnitsky, P. Ginzburg, A. Boag

2020-2025: Israel – USA collaboration Lithium and Sodium Metal Solid State Batteries for Advanced Energy Storage Applications, $1,070,000

2021-2024: On the road to a flexible multi-coaxial-cable 3D printed battery, BSF

Other activities:

2017-present: Member of Teaching Committee - Bachelor's Degree, School of Chemistry, TAU

2018-present: The Raymond and Beverly Sackler Chair in Chemistry and Energy Sciences, TAU

2018-present: Member of Tel Aviv University Committee of Research and Development

2019-present: Member of Committee for Research Students (PhD), School of Chemistry, TAU

2019-present: President of Israel Electrochemical Society

2019-present: Member of Senate, TAU

Summary of work

3D Silicon/Metal-Silicide Anodes for Lithium-Ion Batteries

We study the improved, easy-to-fabricate three-dimensional (3D) Si anodes with enhanced electrochemical stability. The anodes have been prepared by simultaneous application of the following strategies: (i) use of Si nanoparticles (D50 of 100 nm), (ii) use of porous, high-surface-area 3D metal foam current collector, (iii) formation of metal-silicide layer, which bounds Si to the foam. Copper, nickel, and titanium metallic foams as 3D current collectors have been investigated. Silicon nano- and micron-size particles were loaded by electrophoretic deposition (EPD), or ultrasonic (US) agitation. EPD of SiNPs on the foam current collectors was found to result in the formation of silicon layer of different thicknesses and adhesion to the substrate. 3D silicon-on-foam anodes underwent annealing at 350, 500, 750 and 950C and at 1 to 5 hours. The morphology, composition, structure, and electrochemical performance of the 3D Si-on-foam - anodes have been studied. ESEM, and EDX and XRD data confirmed multi-layer structure of the anodes, namely, the bottom layer of metal foam; the top layer, which consists of neat-Si NPs and a metal-silicide layer which is formed in between. XPS measurements support formation of metal silicides and three-layer structure.
Electrochemical tests of Si/NMC cells reveal that the reversible capacities of 3D-Si-metal foam anodes depend on the type of foam, its porosity and on the duration of annealing process. The better performance for Si-on-Cu anode deposited on 500µm-

thick-foam is 300mAh/gSi+silicide. The reversible capacity of 500 mAh/gSi+Silicide after 80 cycles was obtained for Si-Ni anode deposited on 100μm-thick-foam and that of Si-Ti anode on 600μm-thick-foam. 3D Si-on-Ni cathodes demonstrate high C-rate capability. Analysis of the dQ/dV plots shows that at low voltages (~3.77V on charge and ~3.5-3.6V on discharge), the a-LixSi is formed, and at higher voltages (~3.97V- charge and ~3.79V- discharge), the c-Li15Si4 is derived. In addition, alongside the incomplete coating of the bare metal surface, an additional peak at ~4V attributed to Li plating/stripping has been detected, however further investigation of three-electrode cells is needed to unravel the complex mechanism of charge/discharge in NMC/Si-on-foam cells.

We believe that the use of flexible 3D current collectors is a very promising approach due to the high-power capability of the optimized electrodes, and an optional possibility of current collectors to operate as meta-materials for the compensation of continuous volumetric changes occurring in the batteries upon charge and discharge.

Synthesis and electrochemical performance of silicon-nickel nanowire alloy anodes

In order to improve the durability of silicon-nanowire (SiNW) electrodes a core–shell structure composed of SiNW core and a metal silicide layer was created. SiNWs underwent electroless deposition of nickel, followed by annealing at high temperature. The effect of the relative content of nickel salt, complexing and reducing agents on the deposition rate and morphology of the coating was tested. The choice of composition and coating parameters was made to enable conformal and thinnest Ni coating and to ensure that not all the silicon nanowires will be transformed in the following thermal treatment step into fully Ni-silicide NWs.

SEM, TEM and EDS methods show the formation of Ni silicides during the thermal treatment at 900 C. The shell coverage is composed of multiple phases and grains. Examination of the electrochemical performance of the SiNi alloy anodes showed stable electrochemical behavior and high capacity retention compared to the pristine SiNW anode.

Ion transport in plasticized LAGP-based electrolytes

This study presents the development and characterization of a new polymer-in-ceramic electrolyte, fabricated by electrophoretic deposition. Different compositions of the suspension and different EPD parameters were investigated in order to achieve high stability of the suspension and smooth, homogeneous and conformal films. Lithium aluminium germanium phosphate was used as ceramic material, and polyethylenimine– as the charging agent of ceramic particles. It was found that the mass of the deposit increases almost linearly with time and that the deposition time affects the morphology of the deposit. The longer the process, the rougher the surface morphology of the deposited film. Addition of PEI to the acetone-based suspension, not only increased the zeta potential and mobility of the LAGP particles, but also improved adhesion of the film to nickel substrate. The TGA tests showed that despite the fivefold and even tenfold excess of PEI concentration over that of LAGP in the suspension, the content of polymer in the deposited film varies only from 14 to 17%. This observation indicates that the density of the adsorbed PEI chains at a 1:1 LAGP:PEI ratio is sufficient for the charging of ceramic particles. Because of steric and electrostatic hindrance of the adsorbed polymer chains, further increase of PEI concentration is ineffective, but presumably causes higher viscosity. TOFSIMS spectra showed homogeneous lateral distribution of the polymer binder in electrophoretically deposited composite films. From dielectric measurements, only one distinct relaxation process was observed for the LAGP-PEI electrophoretically deposited film at low temperatures. Addition of IL electrolyte resulted in the appearance of several relaxation processes appearing at different frequency and temperature ranges. At low temperatures, the complex dielectric relaxation processes are assigned to the motion of Li^+ cations, through the LAGP grains, along the defective ceramic grain boundaries and via inter-grain and inter-cluster hopping. Low-temperature DC conductivity of LAGP is higher than the conductivity of composite electrolytes containing excess of LiTFSI-IL and plasticized films. Above the glass transition of IL the DC conductivity of plasticized composite electrolyte approaches that of the LAGP powder thus enabling the exchange of lithium cations between superionic ceramics and polymer phase.

In-operando Terahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes

We have found that THz-TDS can detect alterations of the indefinable SEI layer under cycling conditions, and more importantly, during rest periods. By on-line monitoring of the THz reflectivity from the electrode-electrolyte interface within a working electrochemical cell, we were able to identify the SEI formation on the surface of the Si electrode during the lithiation process, and its partial dissolution during prolonged delithiation. Our measurements show that certain parts of the SEI tend to dissolve during rest periods if not fully formed before, demonstrating the importance of efficient complete SEI formation in batteries. The presented technique lays the basis for utilizing terahertz spectroscopy as a uniquely desirable tool in the ever-growing field of operando characterization of electrochemical cells.

Brian Rosen's group

Eliran Hamo	Post-doc
Sukanta Chakrabarrty	Post-doc
Saurav Sorcar	Post-doc
Moran Dahan	PhD Student
Hodaya Zinowitz	MSc Student
Kachal Hirshberg	MSc Student
Bar Favelukis	MSc Student
Rebeca Miyar	MSc Student
Gil Hayoun	Laboratory Engineer
Nofar Basa	MSc Student
Reut Saporta	MSc Student
Shachar Zaltzberg	BSc Student
Nomi Moshe	BSc Student
Sapir Badnani	BSc Student
Tal Meirovich	BSc Student

The group of Brian Rosen made progress in the following areas during 2021:

1. We showed how magnetron sputtering of Ta onto a carbide-based electrode can simultaneously improve its oxygen reduction activity and durability under accelerated stress testing. This improvement came from a protective Ta_2O_5 phase which both prevented Mo_2C oxidation and micro-void formation at the electrode-membrane interface

2. We showed how electrodeposition of Pt onto Mo_2C nanoparticles could be used to synthesize low-dimensional Pt nanostructures (<2nm) with superior metal-support interactions. In order to exploit this advantage, the deposition needs to occur within a specific electrochemical window ~100 mV wide. Deposition above this window will not allow for nuclei formation (growth still possible) and deposition below this window will cause the deposition mechanism to shift to larger 3D structures. Improved Pt-Mo_2C interfaces also showed improvements to mass activity and the ability to maintain a stable surface area after significant electrochemical cycling.

3. We showed how alloying Mo_2C with TaC gave rise to a catalyst support which was simultaneously more active and more stable as an anode in alkaline fuel cells. The improved activity was demonstrated by showing how allowing Mo_2C with other transition metal carbides can modulate the electronic structure of PtRu (EXAFS), as well as DFT calculations showing "volcano plot" behavior where the hydrogen binding energy varied as a function of alloying carbide. This is a relatively new strategy in the AFC world since the majority of studies try to boost activity by modulating the metal catalyst structure – where instead we show that it is possible to achieve this goal by modulating the support phase

4. We showed how thermal treatments and microvoids in 3D printed TiAlV alloys compared with their counterparts prepared by traditional manufacturing methods. Both the mechanical properties and the phase changes at higher temperature are impacted by the use of 3D printing technology

Collaborations

During 2021 we maintained vital collaborations with the following industries:

1. MadeiTaas (Israel)
2. Fonto Power (Israel)
3. Helios (Israel)

During 2021 we maintained vital collaborations with the following researchers

1. Noam Eliaz (TAU)
2. Eyal Sabatani (NRCN)
3. Eitan Tiferet (NRCN)
4. Michael Gozin (TAU)
5. Nissim Navi (NRCN)
6. Yaniv Gelbstein (BGU)
7. Giora Kimmel (BGU)
8. Maya Bar-Sadan (BGU)

9. Idan Hod (BGU)
10. Michal Leskes (WIS)
11. Oswaldo Dieguez (TAU)
12. Peter Voorhees (Northwestern, USA)
13. Chris Wolverton (Northwestern, USA)
14. TRS Prassana (Indian Institute of Technology Bombay)
15. Kyriaki Polychronopoulou (Khalifa University, UAE)

Publications in 2021 (related to the INREP activities):

(1) E. Hamo, R.K. Singh, J.C. Douglin, S. Chen, M. Ben Hassine, E. Carbo-Argibay, S. Lu, H. Wang, P.J. Ferreira, B.A. Rosen# and D. Dekel#
Carbide-supported PtRu Catalysis for Hydrogen Oxidation Reaction in Alkaline Electrolyte
#co-corresponding authors
ACS Catal. **11**, 932-947, *2021*

(2) E.R. Hamo, R. Saporta, B.A. Rosen
Active and Stable Oxygen Reduction Catalyst Prepared by Electrodeposition of Pt on Mo2C at Low Overpotential
ACS Appl. Energy Matter. **4** (3) 2130-2137, *2021*

(3). E. Brosh, N.U. Navi, B.A. Rosen, N. Eliaz, Microvoids in Electrochemically Hydrogenated Titanium-Based Alloys
Int. J. of Hydrog. Energy, **46**, (52), 27234-27242, *2021*

(4). N. Navi, B.A. Rosen, E. Sabatani, J. Tenenbaum, E. Tiferet, N. Eliaz, Thermal decomposition of titanium hydrides in electrochemically hydrogenated EBM and wrought Ti-6Al-4V alloys using in-situ high-temperature XRD
Int. J. of Hydrog. Energy, **46**, (59), 30423-30432, *2021*

(5). E.R. Hamo, B.A. Rosen, Improved Durability and Activity in Pt/Mo_2C Fuel Cell Cathodes by Magnetron Sputtering,
ChemElectroChem, **8**, 3123-3134, *2021*

(6). C. Barad, G. Kimmel, B.A. Rosen, A. Sahartov, H. Hayun, J. Zabicky, Y. Gelbstein, Lattice Variation in Cubic Y_2O_3 in Three Dimensions: Temperature, Pressure, and Crystal Size,
Journal of Alloys and Compounds, 885, 161199, *2021*

(7). N. Lulu-Biton, E. Sabatani, B.A. Rosen, N. Kostirya, G. Agronov, E. Tiferet, N.U. Navi, N. Eliaz
Mechanical Behavior of Electrochemically Hydrogenated Electron Beam Melting (EBM) and Wrought Ti–6Al–4V using Small Punch Test,
Int. J. of Hydrog. Energy, 47 (9) 6388-6403

(8). S. Sorcar, J. Das, E.P. Komarala, L. Fadeev, B.A. Rosen*, Michael Gozin*, Design of Coke-Free Methane Dry Reforming Catalysts by Molecular Tuning of Nitrogen-Rich Combustion Precursors, *Materials Today: Chemistry*
*co-corresponding authors
Materials Today: Chemistry, 24 100765

Special Achievements of the group during 2021

1. Received "Young Innovator Award in Nanocatalysis" by the springer journal Nano Research

2. 1 PhD graduate at 3 MSc graduates

Presentations in international meetings/Events
1) American Chemical Society 2021 Fall Meeting (Catalysis Division- ACS/ICS)
2) Beijing Institute of Technology Summer School
3) Israeli Materials Engineering Conference (IMEC)
4) Manipal University Summer School on Materials Engineering and Energy Sciences
5) TAU-Khalifa University Workshop
6) Workshop on Surface Science of Catalytic Systems (WIS)

List of grants from 2021:

1. Deutch-Israeli Project (DIP), through DFG for investigation of MXene-based materials for energy conversion catalyst (1.55 million Euro) in collaboration with Noam Eliaz, Maxim Sokol from TAU, and Dierk Raabe and Baptiste Gault from Max Plank.

2. Israeli Ministry of Energy project for the production of blue hydrogen via methane pyrolysis using our patented multi-phase molten metal pyrolysis reactor (622,000 NIS)

3. Israeli Ministry of Energy project for the pulsed electrodeposition of platinum on transition metal carbide substrates as a way to lower the loading and increase the activity of carbide-based fuel cell electrodes (420,000 NIS)

4. Gordon Center for Energy Research grant for studying the effect of plasmonic enhanced catalysis using in-situ X-ray diffraction ($10,000)

<u>Work planned to 2022-2023:</u>

1. Determine the ideal pulse parameters to grow low-dimensional Pt structures on Mo_2C substrates to improve upon the ORR mass activity possible reported by our 2021 paper in ACS Applied Energy Materials.
2. Establish a specialty purpose company (SPC) on the basis of the blue hydrogen technology patented by our lab using a multi-phase molten metal reactor. We wish to further lower the activation energy compared to those previously reported in the literature by engineering the environment that the methane bubble experiences.
3. Establish a specialty purpose company (SPC) on the basis of the ammonia production catalysts patented by our lab or start a sponsored project to license and commercialize this exsolution-based technology with the company Topsoe.

4. After having determined the degradation mechanism of MXenes at positive electrochemical potential and the role of tantalum doping, we wish to further reverse-engineer the degradation mechanism and expand the usable electrochemical window for Ti-based MXenes without worrying about degradation
5. Stability the MXene phase at the PEMFC cathode (anode stabilization already accomplished)
6. Establish parameters for a standardized experiment based on X-ray diffraction in order to differentiate between plasmonic and thermal impacts on catalysis utilizing Pd, Au, Cu nanoparticles
7. Utilize machine learning in order to predict a transition metal carbide alloy with the highest possible oxygen binding energy to its surface. Such a material would readily form a protective oxide layer and would maintain both electrochemical activity and stability
8. Exploit strain-based engineering of heterostructures via phase transformations to grow metal-ceramic interfaces which would improve hydrogen production by chemical looping.
9. Study exsolution in ceramics with very high aspect ratios (nanowires)

Amir Natan's group

Current Team Members working on batteries related projects (not only in the framework of the INREP):

First Name	Last Name
Polina	Tereshchuk
Vipin	Kumar
Michael	Murat
Amir	Felestian

Research Topic/s:

1) Simulations of electrode surface reactions for metal-air batteries

2) Molecular dynamics simulations of gases in solvents and electrolytes

3) Faster Molecular Dynamics and quantum methods development

Ultimate Research Goals in the Framework of INREP:

1) Design principles for materials optimization in metal-air batteries
2) Simulation at different scales of processes in metal-air batteries and fuel-cells.

Relevant Instrumentation in your lab:

1) Computer cluster (~1000 cores).

2) DFT and classical MD software tools (e.g. VASP, LAMMPS, and others).

Major Achievements for FY2021:

1) Classical simulations of gases in solvents and electrolytes.
2) Simulation of ORR reactions at metal surfaces
3) Improved deep learning based MD

Plans for FY 2022:

1) Simulation of ORR and other reactions at more complex and diverse surfaces
2) Simulation of solid/liquid electrolyte interfaces.

Relevant Publications 2021:

1. Ronja Haas, Michael Murat*, Manuel Weiss, Jürgen Janek, Amir Natan† and Daniel Schröder†, "Understanding the Transport of Atmospheric Gases in Liquid Electrolytes for Lithium–Air Batteries", Journal of The Electrochemical Society (JES), 168, 070504 (2021)
2. Natasha Ronith Levy, Polina Tereshchuk, Amir Natan, Ronja Haas, Daniel Schröder, Jürgen Janek, Peter Jakes, Rüdiger A Eichel, Yair Ein-Eli, "Hybridization of carbon nanotube tissue and MnO_2 as a generic advanced air cathode in metal–air batteries", Journal of Power Sources, 514, 230597 (2021)
3. Dima Kaplan, Polina Tereshchuk, Chen Olewsky, Liz Keinan, Ohad Ben Yehuda, Meital Shviro, Amir Natan, Emanuel Peled, "Study of Ruthenium-Contamination Effect on Oxygen Reduction Activity of Platinum-Based PEMFC and DMFC Cathode Catalyst", Journal of The Electrochemical Society (JES), 169, 014517 (2022).

Grants 2021:

2020-2024: PAZY grant "Machine Learning based Force Fields for large scale simulations of surfaces and interfaces", ~200KNIS per year, PI: Amir Natan

2019-2022: MOST - German-Israeli Battery and Electrochemistry Research Program, "Liquid Electrolytes for Next-Generation Battery Systems (ELONGATE)", ~200KNIS per year per PI, PIs: Amir Natan (TAU), Yair Ein-Eli (Technion), Juergen Janek (Giessen, Germany).

Summary of work

The group of Amir Natan performs quantum and classical simulations of materials with a focus on energy storage and light-matter interactions. In addition, the group develops methods for fast Density Functional Theory (DFT) calculations on a real-space grid and

Deep Learning (DL) methods for fast and accurate molecular dynamics (MD) simulations. We simulate with DFT reactions at metal, metal-carbide, and metal-oxide electrode surfaces for metal-air batteries and fuel-cells. Specifically, we recently demonstrated good agreement between experimentally measured oxygen reduction potential to calculated oxygen binding energy. In addition, we were able to give a qualitative theoretical prediction for the behavior oxygen reduction reaction (ORR) activity on metal surfaces that are doped with another metal, and to link oxygen binding on metal-oxides to the material behavior as a catalyst. While our focus is mostly metal-air batteries, very similar processes occur in the context of fuel-cells and one of the projects was in fact in this context. Another important aspect of batteries design is the solvents and electrolytes and the diffusion and mobility of oxygen and other molecular species inside them. We simulate with MD the diffusion of oxygen and other gases in pure solvents and also in solvents with different concentration of lithium salts. Initial comparison with experimental measurements shows very good fit between experiment and theory and allows us to build a body of reliable knowledge base for those materials properties. We intend to expand our simulations to additional solvents and electrolytes and to eventually link our measured properties to devices performance. Finally, we continue to develop our DL methods to achieve MD simulations which are close in speed to classical force-field simulations and close in accuracy to quantum calculations. We have recently demonstrated that we get the correct radial distribution functions (RDFs) for MD simulations of sodium and aluminum in a wide range of temperatures and state of matter. In addition, we were able to predict correctly the phonon spectra of those materials and their derived thermal properties. We start to simulate surfaces and intend to progress with this method for the simulations of surface reactions at relatively large surface cells (thousands or tens of thousands of atoms).

Sharly Fleischer's group

Current Team Members:

First Name	Last Name	Position
Soumitra	Hazra	Postdoc
Ran	Damari	PhD (about to finish)
Amit	Beer	PhD
Ivan	Ostrovsky	Direct PhD
Inbar	Sternbach	M.Sc. (starting)
Hana	Tourchinsky	M.Sc. (starting)
Kfir	Rutman	M.Sc. (starting)
Eran	Ben-Arosh	M.Sc. (starting)

Research Topic/s:

1) Operando THz spectroscopy of battery electrodes

2) Characterization and manipulation of Laser-Induced air plasma.
3) Strong coupling in the THz frequency region
4) Coherent rotational control using Near-IR and THz fields
5) Terahertz pulse shaping

Ultimate Research Goals in the Framework of INREP:

1) Development of Operando spectroscopy methods for monitoring the SEI evolution and Lithiation/De-Lithiation during cell cycling
2) Harnessing the intriguing phenomenon of strong-coupling to affect the performance of battery electrodes and interfaces

Relevant Instrumentation in your lab:

1) Amplified ultrashort laser system (oscillator + two-stage amplifier) capable of generating 10mJ, 100/35fs pulses at 1kHz repetition rate
2) Home-built THz reflection spectrometer (+optical pump option)
3) Home-built THz transmission spectrometer
4) Oscillator based home-built THz spectrometer for transmission and reflection spectroscopy with 0.1-3.0THz bandwidth.

Major Achievements (directly related to INREP only):

1) Development of novel In-Operando technique based on THz reflection spectroscopy of batteries throughout their charge-discharge cycling.
2) Spatial super-resolution in THz reflection obtained via optical-pump THz probe setup.

Major collaborations within INREP:

1) Prof. Dina Golodnitsky and her group (In operando THz spectroscopy)
2) Prof. Emanuel Peled and his group (In operando THz spectroscopy)
3) Dr. Michal Leskes and her group (THz spectroscopy of new DNP agents).

Recent Publications 2021:

1. Amit Beer, Ran Damari and Sharly Fleischetr, "Molecular Orientation-Induced Second-Harmonic Generation: Deciphering Different Contributions Apart", J.Phys.Chem.A. 126, 3732 (2022).
2. Daniel Krotkov, Dan Schneier, Svetlana Menkin, Yonatan Horowitz, Emanuel Peled, Diana Golodnitsky and Sharly Fleischer, "Operando Terahertz Spectroscopy of Solid Electrolyte Interphase Ebolution on Silicon Anodes", Batteries & Supercaps, 5, e202100183 (2022). **selected for cover**

3. Maria Kaeek, Ran Damari, Michal Roth, Sharly Fleischer and Tal Schwartz, "Strong Coupling in a Self-Coupled Terahertz Photonic Crystal", ACS Photonics, 8, 1881 (2021).
4. Daniel Krotkov, Eli Flaxer and Sharly Fleischer, "Enhanced Spatial Resolution of Terahertz Spectroscopy via Semiconductor Photoexcitation", OSA Continuum, 3, 3365 (2020).
5. Dina Rosenberg, and Sharly Fleischer, "Intrinsic Calibration of Laser-induced molecular alignment using rotational echoes", Phys. Rev. Research 2, 023351 (2020).
6. Muriel Layani-Tzadka, Daniel Krotkov, Einat Tirosh, Gil Markovich and Sharly Fleischer, "Contact-free Conductivity Probing of Metal Nanowire Films Using THz Reflection Spectroscopy", Nanotechnology, 30, 215702 (2019).
7. Asya Svirinovsky-Arbeli, Dina Rosenberg, Daniel Krotkov, Ran Damari, Krishnendu Kundu, Akiva Feintuch, Lothar Houben, Sharly Fleischer and Michal Leskes, "The effects of sample conductivity on the efficacy of dynamic nuclear polarization for sensitivity enhancement in solid state NMR spectroscopy", Solid State NMR 99, 7-14 (2019).
8. Ran Damari, Omri Weinberg, Natalia Demina, Daniel Krotkov, Katherin Akulov, Adina Golombek, Tal Schwartz and Sharly Fleischer, "Strong Coupling of Light to Collective Terahertz Vibrations in Organic Materials", Nature Communications 10, 3248 (2019).
9. Eli Flaxer and Sharly Fleischer, "Differential Chopping Controller with High-Resolution and Accuracy Using Digital Signal Processor", Rev. Sci. Ins. 90, 076109 (2019).
10. Amit Beer, Dror Hershkovitz, and Sharly Fleischer, "Iris-assisted Terahertz Field-Induced Second Harmonic Generation in Air", Optics Letters 44, 5190-5193 (2019).

Presentations at Conferences 2019:

1) Direct, Spatially Localized Detection of THz-Induced Orientation Dynamics of Gas Phase Molecular Rotors, OTST 2022, Budapest, June 2022.
2) Batteries, Plasmas, Strong Coupling and Molecular Rotors with THz Fields, BIU Physics Colloquium 2022.(Invited)
3) Batteries, Plasmas, Strong Coupling and Molecular Rotors with THz Fields, Quantum Molecular Dynamics Conference, Ein-Gedi, Israel, 2022. (Invited)
4) In-Operando Terahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes, Israel Electrochemical Society Meeting, June 2021. (Invited)
5) Echo Spectroscopy in Multi-level Quantum-Mechanical Rotors, FRISNO 15, Aussois, France, March 2019. (Oral presentation)

6) Strong Coupling of THz Fields to Collective Molecular Vibrations, OASIS 7, Tel-Aviv University, Tel Aviv, Israel, April 2019. (Oral presentation)

7) Terahertz Spectroscopy and Coherent Control of Molecular Dynamics, Ben Gurion University Chemistry department Seminar, Beer Sheva, Israel, May 2019. (Oral presentation)

8) Strong Coupling of Light and Collective Vibrations in Organic Materials at Terahertz Frequencies (poster) + Rotational echo spectroscopy in multi-level molecular rotors (Oral presentation), Gordon Research Conference on Quantum Control of light and matter, Newport, Rhode Island, United states, Aug 2019. (Oral presentation and Poster).

9) In-Operando THz Reflection Spectroscopy of batteries, INREP seminar series, Sep.2020.

<u>Active Grants</u>:

2018-2022 Israel Science Foundation: Basic, yet new decay phenomena in coherent molecular rotations. 1,120,000 NIS.

2022-2026 PAZI - Super-sensitive spatio-temporal characterization of laser-induced plasma using optical diffractometry and intense terahertz fields. 800,000 NIS.

Technion

Yair Ein-Eli's group

A. Review papers published

1. Molecular Engineering Approaches to Fabricate Artificial Solid-Electrolyte Interphases on Anodes for Li-Ion Batteries: A Critical Review, R.G. Fedorov, S. Maletti, C. Heubner, A. Michaelis and **Y. Ein-Eli,** *Adv. Energy Mater.*,**10**, 2101173 (2021).

2. Fast Charging Lithium-ion Batteries: A Review of Materials Aspects, M. Weiss, R. Ruess, P. Minnmann, J. Kasnatscheew, M. Winter, T. Waldmann, M. Wohlfahrt-Mehrens, Y. Levartovsky, D. Aurbach, N. R. Levy, **Y. Ein-Eli*** and J. Janek*, *Adv. Energy Mater.*, **10,** 2101126 (2021).

B. Scientific and Technological papers published

1. Electrochemical and Thermal Behavior of Modified Li and Mn-Rich Cathode Materials in Battery Prototypes: Impact of Pentasodium Aluminate Coating and Comprehensive Understanding of Its Evolution upon Cycling through Solid-State Nuclear Magnetic Resonance Analysis, H. Sclar, S. Maiti, N. Leifer. N. Vishkin, M. F.- Greenstein, M. Hen, J. Grinblat, M. Talianker, N. Solomatin, O. Tiurin, M.

Tkachev, **Y. Ein-Eli**, G. Goobes, B. Markovsky and D. Aurbach, *Adv. Energy & Sustain. Res*., 2000089 (2021).

2. Atomic Layer Deposition (ALD) of Alumina over Activated Carbon Electrodes Enabling a Stable 4 V Supercapacitor Operation, D. Gandla, G. Song, C. Wu, **Y. Ein-Eli*** and D.Q. Tan*, *ChemistryOpen*, **2**, 2000089 (2021).

3. Synergy Effect of Oxygen Plasma and Al_2O_3 Atomic Layer Deposition on Activated Carbon-based Supercapacitor Durability, F. Zhang, **Y. Ein-Eli** and D.Q. Tan, *Front. Energy Res., section Electrochem. Energy Conv. Stor.*, **9**, 124 (2021).

4. Revealing and Excluding the Root Cause of the Electronic Conductivity in Mg-ion $MgSc_2Se_4$ Solid Electrolyte, S. Kundu, A. Kraytsberg and **Y. Ein-Eli**, A*ppl. Mater. Today*, **23**, 100998-16 (2021).

5. A Binary Carbon-free Aluminum Anode for Lithium-ion Batteries, I. Offen-Pollak, M. Auinat, N. Sezin, **Y. Ein-Eli** and Moran Balaish, *J. Power Sources*, **498**, 229902-11 (2021).

6. Surface Stress and Electrochemical Quartz Crystal Microbalance Studies - Exploring the Mechanical Stability of Manganese Oxide as an Oxygen Reduction Reaction Electrocatalyst, O. Keisar, **Y. Ein-Eli** and Y. Cohen *J. Power Sources*, **506**, 230137- 230147 (2021).

7. Enhanced Electrochemical Performance of Supercapacitors via Atomic Layer Deposition of ZnO on the Activated Carbon Electrode Material, C. Wu, F. Zhang, X. Xiao, J. Chen, J. Sun, D. Gandla, **Y. Ein-Eli**, Daniel Q. Tan, *Molecules*, **26**, 4418-4432 (2021).

8. AZ31 Magnesium Alloy Foils as Thin Anodes for Rechargeable Magnesium Batteries, A. Maddegalla, A. Mukherjee, J.A. Blázquez**,** O. Leonet, A.R. Mainar, A. Kovalevsky, D. Sharon, J-F Martin, D. Sotta, **Y. Ein-Eli**, D. Aurbach and M. Noked, *ChemSusChem* **14**, 1-8 (2021).

9. Hybridization of CNTs Tissue and MnO_2 as a Generic Advanced Air Cathode in Metal-air Batteries, N.R. Levy, P. Tereshchuk, A. Natan, R. Haas, **D. Schröder**, J. Janek, P. Jakes, R**.**A. Eichel and **Y. Ein-Eli**, *J. Power Sources.*, **514**, 230597-230609 (2021).

10. Synergistic Air Electrode Combining a Carbon Nanotubes Tissue and Fluorinated Graphite Material in Hybrid Nonaqueous Aluminum Batteries, N.R. Levy and **Y. Ein-Eli**, *J. Solid St. Electrochem.,* **25**, 2759-2766 (2021).

11. Single-Step Synthesis of Nickel Phosphides: Growth Mechanism and Electrochemical Performance, R. Geva, N.R Levy, J. Tzadikov, R. Cohen, M. Weitman, L. Xing, L. Abisdris, J. Barrio, J. Xia, M. Volokh, **Y. Ein-Eli** and M. Shalom, *Mater. Chem A.*, **9,** 27629-27638 (2021).

C. Citation's parameters

a. Number of citations in 2021: 1200

b. H index (as of June 2022, based on Google Scholar): 53

c. Overall No. of citations: 13,100

D. Collaborations

a. **Industrial collaborative with:** RAFAEL and Doral on Li batteries and Zn based chemistry, respectively.

b. **Academic collaboration with:** A. Natan (metal air batteries), D. Aurbach (Li-ion and Mg batteries) and M. Shalom (carbon materials for Na ion batteries), Yoed Tsur (EIS analysis), M. Noked (Mg ion batteries).

E. Number of grad students and senior scientists

a. MSc grad students: 3

b. PhD grad students: 3

c. Senior Scientists: 4

d. Engineers: 2

e. During 2021 2 PhD and 3 MSc students graduated from the group.

F. Funding source

Grant Title	Additional Investigator/s	Funding Source	Starting Date (mm/yy)*	Ending Date (mm/yy)*	Budget ($)
E-MAGIC: European Magnesium Interactive Battery Community		EU H2020 FET Proactive	01-2019	222012-	,000500
Liquid Electrolytes for Next-Generation Battery Systems: Study and implications of Species Solubility and Diffusivity	Amir Natan	MOST	07-2019	06-2022	,000180
Artificial solid electrolyte interphase developed on a single particle Li-ion anode materials via ALD - formation, modifications and detection		GIF	04-2020	02303-2	135,000
Studies of Advanced Lithium-ion Batteries for Electric Vehicles: Modification of Li, Mn-rich Cathode Materials with Surface Coatings via Atomic Layer Deposition	D. Aurbach	ISTRC	07-2021	06-2023	75,000

G. Research accomplishments

1. ALD (alumina) coating stabilizes the carbon electrodes in supercapacitors.
2. ALD (alumina and metal fluoride) coating stabilizes high energy Li-ion cathode materials.
3. Processing conditions of solid-state electrolytes in Mg ion batteries is (again) of high importance.
4. Catalyst exerts stresses under ORR conditions, which can be measured and correlated to the e-chem behaviour.

Dario Dekel' group

Current Team Members working on FC related projects (not only in the framework of the IFCC):

Luba (Kolik) Shmuel	Lab Manager and Researcher
Luba Katzav	Administrative assistant
Leila Reznik	Researcher
Sapir Willdorf-Cohen	PhD student
Syeda Zahan	PhD student
Karam Yassin	PhD student
Songlin Li	PhD student
Yona Lee	PhD student
John Douglin	PhD student
Zihua Chen	PhD student
Maisa Faour	MSc student

Research Topics:

1) PGM-free catalysts for ORR and HOR for AEMFCs
2) Modeling AEMFCs
3) Direct Ammonia HT-AEMFCs
4) Development of new functional groups for Anion Exchange Membranes
5) Development and characterization of Anion Exchange Membranes for FC and EL applications

Relevant Instrumentation in your lab:

RRDE system, Potentiostats, FC test stations, RAMAN, Membrane Test Systems (in-plane and through-plane conductometer), Water uptake automatic apparatus, Glove box, ball mill.

Main Scientific insights and Research accomplishments (in 2021)

HT-AEMFCs

- We are pioneers of this technology, which we started (and coined) during 2020. In 2021 we keep investigating and publishing. We have recently studied the temperature effect on hydroxide diffusion in anion exchange membranes (AEMs). It was found that the OH^- diffusion changes non-monotonically with increasing temperature. Discovery of this unusual temperature dependence of the diffusivity will play an important role in the design of new, stable, highly conducting AEM fuel cell devices.

Direct Ammonia HT-AEMFCs – Experimental and Modeling

- First direct ammonia HT-AEMFCs coupled with PGM-based catalysts was successfully tested at a cell temperature of 80 ^oC and 100^oC. At elevated cell temperature (100^oC), the peak power density and limiting current density were significantly improved.
- OCV increases from 0.5V to 0.75V when the cell temperature goes from 80^oC to 100^oC, indicating the promising benefit from high temperature operating conditions.
- We presented the first 1-D and transient model of AEMFC operated with ammonia fuel, capturing species transport within the cell as well as significant electrochemical reactions taking place in the cell. The model predictions are in good agreement with the experimental data.

Durable AEM for dry and alkaline environments

- We have optimized AEMs, by functionalizing with novel isoindolinium FGs and obtained membranes that are superior to existing commercial. Best results in alkaline fuel cell tests were obtained by connecting isoindolinium to HDPE backbones. We have patented this new FG.

Catalysts

- We have studied and developed Metal-free oxygen reduction reaction (ORR) catalysts of ultra-low cost and high catalytic activity for affordable anion exchange membrane fuel cells (AEMFCs).
- In cooperation with Prof. Natan (TAU), we are working to model the catalyst activity using the first principal density functional theory (DFT) calculation to shed light on the intrinsic kinetic activity.

- We succeed to develop bi-functional doped graphites (I- , S-, N- and B-doped-graphite) as a metal-free catalyst for the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) in alkaline electrolytes.
- The doped graphites showed promising AEMFC performance indicating their potential as cathode catalysts in AEMFCs.

Students (graduates and Postdocs) in 2021:

Completed M.Sc. Theses

Yifan Li (China), **M.Sc.**, "Surface Acoustic Wave Mitigation of Precipitate Deposition on Solid Surfaces". (completed: December **2021**) (co-advisor w. Prof. Manor)

Completed Ph.D. Theses

Nansi Gjineci (Greece), **Ph.D.**, "New kinetically stable quaternary ammonium salts for alkaline fuel cell applications". (completed: Jan **2021**) (co-advisor w. Prof. Diesendruck)

Ph.D. Theses in progress

1. Sapir Willdorf (Israel), direct **Ph.D.** track, "Stability studies of anion conducting ionomeric materials for Anion Exchange Membranes Fuel Cells (AEMFCs)". (started: October 2016) (co-advisor w. Prof. Diesendruck)
2. Karam Yassin (Israel), direct **Ph.D.** track, "Anion exchange membrane fuel cell modelling". (started: October 2017) (co-advisor w. Prof. Brandon)
3. Yona Lee (Korea), **Ph.D.**, "Synthesis and Characterization of Stable AEMs". (started: October 2019)
4. John Douglin (USA), **Ph.D.**, "High-temperature anion-exchange membrane fuel cells". (started: April 2020)
5. Mushrifa Syeda Zahan (India), **Ph.D.**, "TBD". (started: October 2021)
6. Zihua Chen (China), **Ph.D.**, "TBD". (started: October 2021)

M.Sc. Theses in progress

1. Saja Bsoul (Israel), **M.Sc.**, "Stability of anion exchange membranes". (started: October 2018)
2. Ziye Xiao (China), **M.Sc.**, "Electrocatalysts for AEMFCs". (started: October 2019)
3. Songlin Li (China), **M.Sc.**, "Anion exchange membrane characterization for high-temperature applications". (started: October 2019)
4. Lanjie Jiang (China), **M.Sc.**, "Anion exchange membranes fuel cell performance". (started: October 2019)
5. Maysa Faour (Israel), **M.Sc.**, "Electrochemical separation of oxygen". (started: October 2021)
6. Zhicong Liang (China), **M.Sc.** at Guandong-Technion University (GTIIT), China, "Development of facilitated transport membrane for CO_2 removal for

H_2-Air fuel cells". (started: October **2021**) (co-advisor w. Prof. Xuezhong He at GTIIT, China)

Supervision of Postdoctoral fellows

Dr. Ramesh Singh (India), Started: November 2018

Citations (2021): 1451, **(2022, until June)**: 930, **H index**: 36

Publications (in 2021)

1. "Electroreduction of oxygen on cobalt phthalocyanine-modified carbide-derived carbon/carbon nanotube composite catalysts"; Reio Praats, Maike Käärik, Arvo Kikas, Vambola Kisand, Jaan Aruväli, Päärn Paiste, Maido Merisalu, Ave Sarapuu, Jaan Leis, Väino Sammelselg, John Douglin, Dario R. Dekel, and Kaido Tammeveski; J. Solid State Electrochem. 25, 57-71, **2021**. (IF=2.5)
2. "Carbide-supported PtRu catalysts for hydrogen oxidation reaction in alkaline electrolyte"; Eliran R. Hamo, Ramesh K. Singh, John C. Douglin, Sian Chen, Mohamed Ben Hassine, Enrique Carbo-Argibay, Shanfu Lu, Haining Wang, Paulo J. Ferreira, Brian A. Rosen, and Dario R. Dekel; ACS Catalysis 11, 932-947, **2021**. (IF=12.3)
3. "Transition-metal and nitrogen-doped carbide-derived carbon/carbon nanotube composites as cathode catalysts for anion-exchange membrane fuel cells"; Jaana Lilloja, Elo Kibena-Põldsepp, Ave Sarapuu, John C. Douglin, Maike Käärik, Jekaterina Kozlova, Päärn Paiste, Arvo Kikas, Jaan Aruväli, Jaan Leis, Väino Sammelselg, Dario R. Dekel, and Kaido Tammeveski; ACS Catalysis 11, 1920-1931, **2021**. (IF=12.3)
   # Over 25 citations in the first year (source: Google Scholar)
4. "An anion-exchange membrane fuel cell containing only abundant and affordable materials"; Jasper Biemolt, John C. Douglin, Ramesh K. Singh, Elena S. Davydova, Ning Yan, Gadi Rothenberg, and Dario R. Dekel; Energy Technology 9, 2000909, **2021**. (IF=3.2)
5. "Atomistic Insights into the Hydrogen Oxidation Reaction of Palladium-Ceria Bifunctional Catalysts for Anion-Exchange Membrane Fuel Cells"; Sanjubala Sahoo, Dario R. Dekel, Radenka Maric, and S. Pamir Alpay; ACS Catalysis 11, 2561-2571, **2021**. (IF=12.3)
6. "Crosslinked quaternary phosphonium-functionalized poly(ether ether ketone) polymer-based anion-exchange membranes"; Mamta Kumari, John C. Douglin, and Dario R. Dekel; J. Membrane Science 626, 119167, **2021**. (IF=8.7)
7. "Porphyrin aerogel catalysts for oxygen reduction reaction in anion-exchange membrane fuel cells"; Noam Zion, John C. Douglin, David A. Cullen, Piotr Zelenay, Dario R. Dekel, and Lior Elbaz; Adv. Functional Mater. 31(24), 2100963, **2021**. (IF=16.8)

8. “Effect of the synthetic method on the properties of Ni-based hydrogen oxidation catalysts”; Elena Davydova, Maidhily Manikandan, Dario R. Dekel, and Svein Sunde; ACS Appl. Energy Materials, 4, 3404−3423, **2021**. (IF=4.5)
9. “Ligand Valency Effects on the Alkaline Stability of Metallopolymer Anion-exchange Membranes”; Kanika Aggarwal, Saja Bsoul, John C. Douglin, Dario R. Dekel, and Charles E. Diesendruck; Macromolecular Rapid Commun. 42(16) 2100238, **2021**. (IF=4.9)
10. “Metal nanoparticles entrapped in metal matrices”; Dina Pinsky, Noam Ralbag, Ramesh K. Singh, Meirav Mann-Lahav, Gennady E. Shter, Dario R. Dekel, Gideon S. Grader, and David Avnir; Nanoscale Adv. 3, 4597-4612, **2021**. (IF=4.6)
11. “A High-Temperature Anion-Exchange Membrane Fuel Cell with a Critical Raw Material-free Nitrogen-doped Carbon Cathode”; John C. Douglin, Ramesh K. Singh, Saja Haj, Songlin Li, Jasper Biemolt, Ning Yan, John R. Varcoe, Gadi Rothenberg, and Dario R. Dekel; Chemical Engineering J. Adv. 8, 100153, **2021**.
12. “Bifunctional Oxygen Electrocatalysis on Mixed Metal Phthalocyanine-Modified Carbon Nanotubes Prepared via Pyrolysis”; Yogesh Kumar, Elo Kibena-Põldsepp, Jekaterina Kozlova, Mihkel Rähn, Alexey Treshchalov, Arvo Kikas, Vambola Kisand, Jaan Aruväli, Aile Tamm, John C. Douglin, Scott J. Folkman, Ilario Gelmetti, Felipe A. Garcés-Pineda, José Ramón Galán-Mascarós, Dario R. Dekel, and Kaido Tammeveski”; ACS Applied Materials & Interfaces 13, 35, 41507-41516, **2021**. (IF=9.2)
13. “Multi-scale study on bifunctional Co/Fe–N–C cathode catalyst layers with high active site density for polymer electrolyte fuel cells”; Weikang Zhu, Yabiao Pei, John C. Douglin, Junfeng Zhang, Haoyang Zhao, Jiandang Xue, Qingfa Wang, Ran Li, Yanzhou Qin, Yan Yin, Dario R. Dekel, and Michael D. Guiver; Applied Catalysis B: Environmental 299, 120656, **2021**. (IF=19.5)
14. “A surprising relation between operating temperature and stability of anion exchange membrane fuel cells”; Karam Yassin, Igal G. Rasin, Sapir Willdorf-Cohen, Charles E. Diesendruck, Simon Brandon, and Dario R. Dekel; J. Power Sources Adv. 11, 100066, **2021**.
15. “Understanding how Single-Atom Site Density Drives the Performance and Durability of PGM-Free Fe-N-C Cathodes in Anion Exchange Membrane Fuel Cells”; Horie Adabi, Pietro Giovanni Santori, Abolfazl Shakouri, Xiong Peng, Karam Yassin, Igal Rasin, Simon Brandon, Dario R. Dekel, Noor Ul Hassan, Moulay-Tahar Sougrati, Andrea Zitolo, John R. Varcoe, John R. Regalbuto, Frédéric Jaouen, and William E. Mustain; Materials Today Adv. 12, 100179, **2021**. (IF=7.6)
16. “Surface acoustic wave mitigation of polymer deposition – An active self-cleaning surface”; Yifan Li, Dario R. Dekel, and Ofer Manor; ACS Appl. Mater. Interfaces 13, 49, 59471-59477, **2021**. (IF=9.2)

Collaborations (local and international)

1. Prof. Elisabete Santiago (Instituto de Pesquisas Energéticas e Nucleares, Brazil)
2. Prof. Patric Jannasch (Lund University, Sweeden)
3. Prof. Toshihide Horikawa (Tokushima University, Japan)
4. Prof. Sanjeev Mukerjee (Northeastern University, USA)
5. Prof. Matthew W. Liberatore (University of Toledo, USA)
6. Prof. Marian Chatenet (Universit Grenoble Alpes, France)
7. Prof. Maric Radenka (University of Connecticut, USA)
8. Prof. Simon Brandon (Technion, Israel)
9. Prof. William E. Mustain (University of Connecticut, USA)
10. Prof. Steven Holdcroft (Simon Fraser University, Canada)
11. Prof. Serhiy Cherevko (Julich, Germany).
12. Prof. Jasna Jankovic (University of Connecticut, USA)
13. Prof. Chulsung Bae (Rensselaer Polytechnic Institute, USA)
14. Prof. Mark E. Tuckerman (New York University, USA)
15. Prof. Charles E. Diesendruck (Technion, Israel)
16. Prof. Nir Gavish (Technion, Israel)
17. Prof. Ulrike Krewer (Braunsweig Technische University, Germany)
18. Prof. John Varcoe (University of Surrey, UK)
19. Prof. Gideon S. Grader (Technion, Israel)
20. Prof. David Avnir (Hebrew University, Israel)
21. Dr. Bryan Pivovar (National Renewable Energy Laboratory, USA)
22. Prof. Simcha Srebnik (UBC, Canada)
23. Prof. Svein Sunde (Norwegian University of Science and Technology, Norway)
24. Dr. Alejandro Oyarce Barnett (SINTEF, Norway)
25. Dr. Hamish A. Miller (CNR-ICCOM, Italy)

Collaborations inside INREP

1. Prof. Yair Ein-Eli (Technion, Israel)
2. Prof. Brian Rosen (Tel Aviv University, Israel)

3. Prof. Slava Freger (Technion, Israel)
4. Prof. Ilya Grinberg (Bar-Ilan University)
5. Prof. David Eisenberg (Technion, Israel)
6. Prof. Lior Elbaz (Bar-Ilan University, Israel)
7. Prof. Yoed Tsur (Technion, Israel)
8. Prof. Gidi Grader (Technion, Israel)
9. Prof. David Zitoun (Bar-Ilan University)
10. Prof. Amir Natan (Tel Aviv University)

Conferences (in 2021)

Invited talks in international conferences and workshops

1. Dekel D. R., "Alkaline Stability of Anion-Exchange Membranes"; **Invited Keynote** Speaker at the Solid State Proton Conductors 20 (SSPC-20), Lund University (online), Sweden, September 27-October 1, **2021**.

2. Dekel D. R.; "Anion-Exchange Membrane Fuel Cells – the Next Frontier; **Invited** speaker at the 240th ECS Meeting, (online) Orlando, USA, October 10-14, **2021**.

3. Dekel D. R., "Current Challenges in Anion-Exchange Membrane Fuel Cells"; **Invited** speaker at Lorentz Center Workshop on Electrifying Chemistry: from fundamentals to industrial application; Leiden, Netherlands, November 22-26, **2021**.

Active research grants (in 2021)

Duration (years)	Title & Funding source	Funding
2016-2021	Israel Fuel Cell Center (IFCC) Prime Minister Office (through INREP2)	$263,000
2017-2021	"Novel composite ionic-electronic conducting electrocatalytic materials for advanced fuel cells" Israel Science Foundation (ISF) - Individual Research Grant	$394,000
2017-2021	"Research equipment for preparation, characterization and testing of electrochemical devices for energy generation and storage"; Israel Science Foundation (ISF) - New-faculty Equipment Grant	$290,000
2019-2021	"Hydrogen oxidation and oxygen reduction reaction catalysts for anion exchange membrane fuel cell	$20,000

	electrodes" Projects de Recherche Conjoints – PRC 2019-2021(Joint Research Projects) Centre National de la Recherche Scientifique (CNRS) & Ministry of Science, Technology and Space (MOST), Total grant: $38,000	
2019-2021	"Water and carbon dioxide in low hydration anion exchange membranes: Resolving the chemistry of membrane stability and hydroxide conductivity for fuel cells applications" US–Israel Binational Science Foundation (BSF) – Regular, Total grant: $230,000	$115,000
2020-2021	"Development of ultra-low-cost oxygen reduction catalysts for anion exchange membrane fuel cell" Israeli Ministry of Energy and Water Resources	$174,000
2021-2022	"Solar Energy Storage using Unitized Anion Exchange Membrane Fuel Cell" The Mauerberger Foundation Fund, Research Award for Transformative Technologies for Africa ("MFF Research Award")	$180,000
2021-2022	"Practical anion-exchange membranes using stable isoindolinium salts" Startup Program Call 2020, Israeli Ministry of Energy	$170,000
2021-2022	"Direct Ammonia High-Temperature Anion Exchange Membrane Fuel Cell", Israeli Ministry of Energy and Water Resources	$140,000
2021-2022	"Design of Nanometric Enzyme-Inspired Catalytic Sites for "N-fuels" Fuel Cells" RBNI NEVET – Call for Hydrogen Technologies, Technion, Total grant: $40,000	$20,000

Yoed Tsur's group

Current Team Members working on INREP related projects:

First Name	Last Name
Gal	Avioz-Cohen
Arthur	Doroshev (graduated)
Rinat	Attias
Vijaya	Sankar
Sioma	Baltianski
Irena	Levin

Research Topic/s:

1) Study of various electrochemical devices including PEM, AFC, SOFC, solid state LIB using Impedance Spectroscopy by Genetic Programming (ISGP)
2) Degradation studies and analysis of PEM systems
3) Development of in operando techniques for fuel cells
4) Development of OER/HER catalysts

Ultimate Research Goals in the Framework of the IFCC:

Adjustment of the ISGP tool for generic use within the fuel cells field, with emphasis on durability\ state of health studies.

Relevant Instrumentation in your lab:

1) Fuel cell test station by Scribner Associates with MFC system and multi-gas abilities.
2) Potentiostats, FRA.
3) High temperature test station.

Major Achievements for FY2021:

1) Development of negative effective resistance module for ISGP, which can help in analyzing and understanding cases that were attributed in the past to non-physical inductance.
2) Improving the function of pseudo-delta in ISGP to better distinguish it from a narrow Gaussian and the like.
3) Acquired techniques for fabricating small SOFC based on doped ceria on Si wafers, which may be compatible with the electronics industry.
4) Progress toward evaluation of the oxygen evolution reaction kinetics of nickel based electro-catalysts by distribution function of relaxation times modelling.
5) Studying the electrochemical OER kinetics of Fe_3S_4@Ni_3S_2 using distribution function of relaxation times analysis.
6) Development of a typical distribution function of relaxation times model for PEM fuel cells.
7) Study of electrical properties of doped $La_2Mo_2O_9$ electrolyte for intermediate-temperature solid oxide fuel cells.

Go/no-Go points:

n/a

Plans for FY 2022:

1) Study of the influence of airborne contaminants on the degradation of PEMFC cathodes: N_2O; summary of CO_2.

2) Cooperation with various groups within INREP on analyzing EIS data.

3) Study of aerogels for catalysis.

Which components developed in your lab in recent years can be implemented in a fuel cell today (also include scale in size and weight when relevant):

1) Impedance Spectroscopy by Genetic Programming (ISGP) software nowadays can be used for study of new materials, processes and components in the fuel cells field and also for in operando degradation interpretation.

Relevant Publications 2021:

1. B. Malik, K.V. Sankar, R. Konar, Y. Tsur, G.D. Nessim, Determining the Electrochemical OER Kinetics of Fe3S4@Ni3S2 Using Distribution Function of Relaxation Times, *ChemElectroChem*, 8, 517 – 523 (2021).

2. W. Moschkowitsch, S. Gonen, K. Dhaka, N. Zion, H. Honig, Y. Tsur, M. Caspary Toroker, L. Elbaz, Bifunctional PGM-free metal organic frameworks-based electrocatalysts for alkaline electrolyzers: trends in the activity with different metal centers, *Nanoscale*, 13, 4576–4584 (2021)

3. R. Attias, K.V. Sankar, K. Dhaka, W. Moschkowitsch, L. Elbaz, M. Caspary Toroker, Y. Tsur, Optimization of Ni-Co-Fe based catalysts for oxygen evolution reaction by surface and relaxation phenomena analysis, *ChemSusChem*, 14, 1737–1746 (2021).

4. G. Avioz-Cohen, D. Gelman, Y. Tsur, Development of a typical distribution function of relaxation times model for PEM fuel cells and quantifying the resistance to proton conduction within the catalyst layer, *J. Phys. Chem. C*, 125, 22, 11867–11874 (2021)

5. T. Paul, Y. Tsur, Influence of isovalent 'W' substitutions on the structure and electrical properties of $La_2Mo_2O_9$ electrolyte for intermediate-temperature solid oxide fuel cells, *Ceramics*, 4, 502–515 (2021)

6. B. Malik, K. V. Sankar, S. K. T. Aziz, S. Majumder, Y. Tsur, G. D. Nessim, Uncovering the change of catalytic activity during the electro oxidation of urea: answering over isolating the relaxation phenomena, *J. Phys. Chem. C*, 125, 23126-23132 (2021).

7. A.K. Baral, Y. Tsur, Electro-Chemo-Mechanical Properties of Gd and Pr-doped Ceria Studied by Temperature Modulated Dilatometry, *J. Eur. Ceram. Soc.*, 42, 2299-2306 (2022).

Grants 2021:

2018-2021: Controlling Defects in Oxide Materials for Water Splitting Devices (250,000 NIS p.a.) (with M. Caspary-Toroker (coordinator), MSc&E and L. Elbaz, BIU), Funding Agency: Ministry of Infrastructure and Energy

2019-2022: Flash sintering of MgO (with NRCN) (240,000 NIS p.a.)

Funding Agency: Pazy Foundation

2020-2023: Low-T SOFC on large membranes by standard Si-fabrication processes (250,000 NIS p.a.) (with I. Lubomirsky, Weizmann)

Funding Agency: Ministry of Infrastructure and Energy

2021-2022, Quantum Nevet Research Grant, The effect of defects on flicker noise in materials for superconducting qubits (with M. Caspary-Toroker (coordinator), MSc&E), $40,000.

2022-2025, Ministry of Infrastructure and Energy, Production of low-cost green hydrogen using catalists based on transition metal aerogels, (with M. Caspary-Toroker (coordinator), MSc&E and L. Elbaz, BIU), 210,000 NIS p.a.

Other activities:

2016-, Director, Grand Technion Energy Program (GTEP).

2014-, member, International Committee of Electroceramics

2014-, editorial board, Journal of Ceramic Science and Technology. Göller Verlag GmbH (publication of the German Ceramic Society, DKG).

2015-, editorial board, Solid State Ionics, Elsevier.

2018- Member of the steering committee of INREP.

Summary of work

We have made progress in our main activity around the area of using advanced EIS analysis to study degradation processes of PEM cathodes. In the case of degradation due to NO we have also identified a potential mitigation strategy.

We have improved ISGP and made it better suited for cases were there are "inductive loops" (which in fact has nothing to do with inductance). Other improvements were made to gain better accuracy and faster runtime at the same time.

ISGP has been implemented on several systems in cooperation with other members of INREP\IFCC.

Zeev Gross's group

First Name	Last Name		E-mail
Amit	Kumar	Postdoc	amitkur@iitk.ac.in
Atif	Mahammed	PhD, Senior researcher	chatif@technion.ac.il
Amir	Mizrahi	PhD, Senior researcher	amirmizrachi@gmail.com
Irena	Saltsman	PhD, Senior researcher	chira@ch.technion.ac.il
Arik	Raslin	PhD student	raslin.arik@campus.technion.ac.il
Sachin	Kumar	PhD student	ksachin@campus.technion.ac.il

The group of Zeev Gross made progress in the following areas during 2021:

Fuel Cells: We prepared corroles that are substituted by either two or three -CF_3 groups at *meso*-carbon position on the corrole macrocycle (Figure 1). These corroles were metalated by first-row non-precious transition metals: cobalt and iron. The -CF_3 groups are electron-withdrawing, and they shift the redox potentials positively even more than pentafluorophenyl groups. These results suggest the possibility to shift the onset potential of these catalysts to more positive direction and thus lower the overpotentials for ORR. Meantime, we found that adsorption of these corroles onto carbon nanoparticles are much more facile and we are currently continuing the measurements of their ability to catalyze ORR under heterogeneous conditions.

We also prepared corrole without any substituents on its macrocycle (Figure 1, parent corrole) and inserted different metals to its core. We fully characterized these compounds including X-ray structures (Figure 1). Figure 2 shows spontaneous absorption from solutions of *meso* substituted pentafluorophenyl groups (left), trifluoromethyl groups (middle) and the novel "parent" metallocorroles, as determined by recording the UV-vis spectra of the solutions before and after the addition of a Vulcan XC72R carbon. The adsorption of these corroles on Vulcan XC72R carbon were size dependent indeed. The smallest one was totally adsorbed while the biggest one was least adsorbed on the carbon nanoparticles. We will study the performance of these novel parent metallo-corroles for ORR and for HER under heterogeneous and homogeneous conditions.

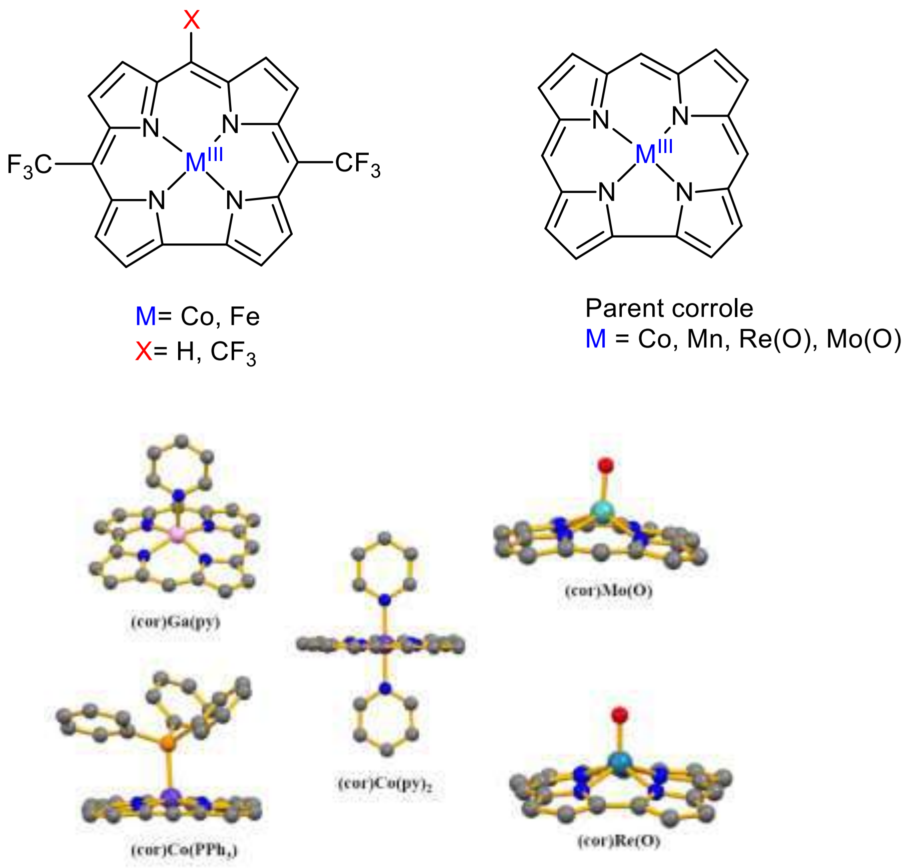


Figure 1. Chemical structures of metallocorroles substituted by trifluoromethyl groups and without any substituents (parent corrole) and the X-ray structures of metallo-parent corrole.

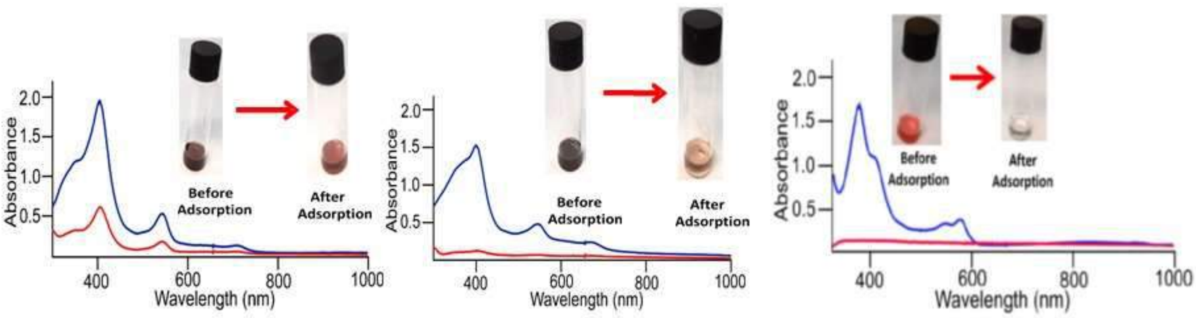
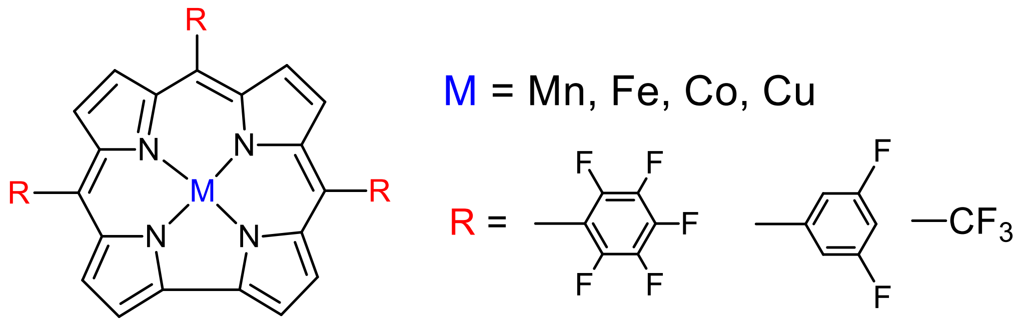


Figure 2. Spontaneous absorption from solutions of *meso* substituted pentafluorophenyl groups (left), trifluoromethyl groups (middle) and "parent" metallocorroles (0.8 mg each, in 1 mL isopropanol), checked by recording the UV-vis spectra of the solutions before and after the addition of a Vulcan XC72R carbon (10 mg).

Redox Mediators for Li-O_2 batteries: We found that among a series of corrole-chelated copper complex the one substituted by 2,6-difluorophenyl on the *meso*-carbon position of the corrole skeleton is the most stable and best performing redox mediator for lithium oxygen batteries. This was achieved by taking advantage of the facile methods for introducing changes in the corrole ligands and by choosing properly the central transition metal cation, two aspects that allow for adjusting the redox properties of the metal complexes for the operative voltage window. This finding will promote the search for superior selection of redox mediators for lithium-oxygen batteries.



Collaborations

Collaborations within INREP

1. With David Eisenberg, from the Technion, on metallocorroles as electrocatalysts for ORR.
2. With Prof. Doron Aurbach, from Bar Ilan University, on redox mediators and oxygen shuttles for efficient charging of Lithium-Oxygen batteries.

Collaborations outside INREP

1. With Prof. Abhishek Dey from School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata, India. The aim of the collaboration is to study earth abundant metal complexes as electrocatalysts for energy relevant processes.
2. With Prof. Tim Bender, Department of Chemistry, University of Toronto, Canada. The aim of the collaboration is to engineer new materials for application in organic solar cells, as well as for proton-to-hydrogen (HER) electrocatalysis.
3. With Prof. Jianzhang Zhao from School of Chemical Engineering, Dalian University of Technology, China. The aim of the collaboration is to study reaction intermediates relevant to catalysis by earth abundant metal complexes with unique and tunable photophysical properties.

4. With Prof. Sankar Prasad Rath, Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, India. The aim of the collaboration is to prepare Mono and bimetallic corrole complexes for energy-relevant photocatalysts.

Collaborations not directly related to INREP activities:

1. With Prof. Tim Storr, Department of Chemistry, University Drive, Canada. The aim of the collaboration is to study the effect of metallocorroles on amyloid aggregations.
2. With Prof. Harry B. Gray, California Institute of Technology, Pasadena, CA, USA. The aim of the collaboration is to study the photophysical properties of metallocorroles.
3. With Prof. John Termini, City of Hope, Duarte, CA, USA. The aim of the collaboration is to use metallocorroles as anti-cancer drugs.

Most Relevant Publications, 2020-2021:

- "Dimeric Corrole Analogs of Chlorophyll Special Pairs", V. K. Sharma, A. Mahammed, A. Mizrahi, M. Morales, N. Fridman, H. B. Gray and Z. Gross. *J. Am. Chem. Soc.* **2021**, *143*, 9450–9460.
- "Hydrogen Evolution Catalysis, by Terminal Molybdenum-Oxo Complexes", P. Yadav, I. Nigel-Etinger, A. Kumar, A. Mizrahi, A. Mahammed, N. Fridman, S. Lipstman, I. Goldberg, and Z. Gross . *Iscience* ***2021**, 24, 102924*
- "Chromophore-Supported Structural and Functional Model of Dinuclear Copper Enzymes, for Facilitating Mechanism of Action Studies",Q. C. Chen, N. Fridman, B. Tumanskii and Z. Gross *Chem. Science* **2021**, *12,* 12445-12450.
- "Corroles: The Hitherto Elusive Parent Macrocycle and its Metal Complexes", A. Kumar, P. Yadav, M. Majdoub, I. Saltsman, N. Fridman, S. Kumar, A. Kumar, A. Mahammed and Z. Gross, *Angew. Chem.* **2021**, *60*, 25097-25103.
- "Controllable and Stable Organometallic Redox Mediators for Lithium Oxygen Batteries", J. Kwak, A. Mahammed, H. Kim, T. T. Nguyen, Z. Gross, D. Aurbach and Y.-K. *Materials Horizons* **2020**, *7*, 214-222.
- "Copper Complexes of CF_3-Substituted Corroles for Affecting Redox Potentials and Electrocatalysis", Sudhakar, A. Mahammed, Q.-C. Chen, N. Fridman, B. Tumanskii and Z. Gross *ACS Appl. Energy Mater.* **2020**, *3*, 2828-2836.
- "Water Oxidation Catalysis by Mono- and Binuclear Iron Corroles", W. Sinha, A. Mahammed, N. Fridman and Z. Gross *ACS Catal.* **2020**, *10*, 3764-3772.

- "Enhanced Synthetic Access to Tris-CF_3-Substituted Corroles", P. Yadav, S. Khoury, A. Mahammed, M. Morales, S. C. Virgil, H. B. Gray and Z. Gross *Org. Lett.* **2020**, *22*, 3119-3122.
- "Elucidation of Factors That Govern the $2e^-/2H^+$ *vs.* $4e^-/4H^+$ Selectivity of Water Oxidation by a Cobalt Corrole", B. Mondal, S. Chattopadhyay, S. Dey, A. Mahammed, K. Mittra, A. Rana, Z. Gross, A. Dey *J. Am. Chem. Soc.*,**2020**, *142*, 21040-21049.

Special Achievements of the group during 2021

1. One student completed his PhD work during 2021, submitted theses.
2. One student completed his MSc work during 2021, submitted theses.
3. Published 11 papers during 2021in highly cited Scientific Journals.

Presentations in relevant international meetings/Events:

2020: There were no conferences because of the Covid

20221: Except for the last conference, all the conferences were virtual

*ICPP, 17.06.2021 "*The Smaller the Better? Synthesis and Properties of Minimally Substituted Corroles*"

*CatMeet, 11-13.10.2021, *"Energy Relevant Electrocatalysis by Metal Complexes of Minimally Substituted Corroles*"

*CCE-2021 SF, 22.02.2021, "*From Homogenous to Heterogenous Energy-Relevant Electrocatalysis by Substituent-Free N4 Macrocyclic Metal Complexes*"

*S. Korea, 18.03.2021 "*Groups 13/14 Elements (& 15) Chelated by Corroles*"

* Prof. Lechosław Latos-Grażyński's 70th Birthday Symposium, Poland, 17-18.9. 2021, "*The journey toward less substituted corroles and sapphyrins*"

*15-23.12.2021: Pacifichem 2021: A Creative Vision for the Future, "Success and surprises in the syntheses of new generation corroles"

List of grants in 2021 and 2022:

Research Topics	Funding Agency	Total grant
Mono and bimetallic complexes for energy-relevant photocatalysts	Indian-Israel joint research cooperation	NIS 200,000

Uniquely designed Molecular Catalysts for Facile Incorporation into Porous Carbon Support	Ministry of Energy	NIS 675,000
Photo- and Electro-Catalysis by Novel Macrocycle Chelates for Energy Relevant Processes	The Pazy foundation	NIS 600,000

Work planned to 2022-2023:

1) Concerning the synthesis of novel class of corroles as catalysts for ORR. We will optimize the synthesis of the corrole without any groups at the *meso*-C atoms and β-pyrrole positions (parent corrole). We will also optimize the preparation of non-precious and earth-abundant first row transition metal complexes of this corrole and insert new ones such as iron, chromium, and copper. We will also compare the reactivity/selectivity for ORR and the absorption on carbon nanoparticles of these totally non-substituted corrole relative to other known corroles. These new corroles will be studied as electrocatalysts for HER as well.

2) Continuing the collaborating on lithium/oxygen batteries project as well, with Prof. Doron Aurbach. We will continue supplying metallocorroles, mainly copper complexes of the newest corroles, as redox mediators.

Viatcheslav Freger's group

Current Team Members working on FC related projects in **2021-2022** (fully or partly in the framework of the IFCC):

Viatcheslav Freger	Prof.
Mikhail Stolov	PhD researcher
Vadim Neklyudov	Postdoc
Jian Li	PhD student
Michael Zelner	PhD student
Aleksandr Leontev	PhD student
Ariel Odess	MSc student
Kejing Li	MSc student

Slava Freger's group made progress in the following areas during 2021:

1. We extended our work on preparation of highly conductive electrospun PEMFC membranes with through-plane conductive channel-orientation to optimize Nafion:PVDF ratio for maximal conductivity.
2. We developed a new procedure for thermally induced controlled fusion of Nafion-PVDF nanofiber composite to overcome membrane durability problems found during testing at Prof Elbas's lab (BIU). This procedure is implemented in a new fusion process and setup for preparing membrane with improved integrity.
3. We introduced and implemented improved measurement setup and protocols for overcoming the challenge of accurately assessing ultra-low through-plane conductivity, highly important for understanding composites with anisotropic characteristics. We also combined the measurements with SAXS and 3D swelling to assess anisotropcity of structure, conductivity and swelling of such composites.
4. We collaborated with Prof Dekel's group (Technon) in developing novel electropolymerized ultra-thin anion-conducting membranes and the use of impedance spectroscopy for their characterization.
5. We collaborated with Prof Frei group (Mat Sci & Eng, Technion) on chearacterization novel materials with mixed electronic-ionic conductivity using electrochemical QCM.
6. In collaboration with Prof. Ulbricht's group (Essen, Germany), we developed novel Nafion-polyamine composite membrane for improved mono-/divalent ion selectivity. We employed this novel material to unravel ion transport mechanism in polyelectrolyte complex membranes.
7. We also develop new models for ion transport in ion-conducting materials in collaboration with Prof Nit (BGU)

Collaborations (2021-2022)

During 2021 we collaborated with

1. Tortech (Israel) on CNT material
2. Academic collaborations with within INREP with Dario Dekel and Lior Elbaz on FC membranes and their characterization
3. Outside INREP – Prof. Gitti Frei (Technion), Prof Zussman (Technion), Dr Yair Cohen (KAMAG), Prof Oded Nit (BGU), Prof. Mathias Ulbricht (UDE, Germany), Prof. Alex Noy (LLNL, USA), Prof. Meni Wanunu (Northeaster U, USA), Prof Alexei Lapkin (Cambridge, UK)

Our work is very well documented in relevant papers and grants received

Publications in 2021-2022:

(1) A. Leontev, R. Bar-On, M. Bass, M. Jurić, C. Schmetz, V. Freger, Spatial pattern and surface-specificity of particle and microorganism deposition and attachment: Modeling, analytic solution and experimental test, *J. Colloid Interface Sci.*, 584 (2021) 45-56.

(2) V Neklyudov, V Freger, Water and Ion Transfer to Narrow Carbon Nanotubes: Roles of Exterior and Interior, *J. Phys. Chem. Lettr.*, 12 (2020) 185-190

(3) H. Frankenstein, E. Stein, M. Stolov, M. Koifman, V. Freger, G.L. Frey. Blends of Polymer Semiconductor and Polymer Electrolyte for Mixed Ionic and Electronic Conductivity, *J. Mat. Chem. C,* in press

(4) RY Li, ZS Wang, ZY Yuan, Constance Van Horne, Viatcheslav Freger, M Lin, RK Cai, JP Chen, A comprehensive review on water stable metal-organic frameworks for large-scale preparation and applications in water quality management based on surveys made since 2015, *Critical Rev Environ. Sci,Technol* (2021) 1-34

(5) A Odess, M Cohen, J Li, M Dantus, E Zussman, V Freger, Electrospun Ion-Conducting Composite Membrane with Buckling-Induced Anisotropic Through-Plane Conductivity, *ACS Applied Materials & Interfaces* 13 (2021) 35700-35708

(6) M. Zelner, P. Jahn, M. Ulbricht, V. Freger, A Mixed-Charge Polyelectrolyte Complex Nanofiltration Membrane: Preparation, Performance and Stability, *J. Membrane Sci.*, 6363 (2021) 119579

(7) V. Freger, G. Ramon, Polyamide desalination membranes: Formation, structure, and properties, *Progress in Polymer Science*, 122 (2021) 101451

(8) YS Oren, V Freger, O Nir, New compact expressions for concentration-polarization of trace-ions in pressure-driven membrane processes, *J. Membr. Sci. Lettr.* (2021) 100003

(9) V Neklyudov, V Freger, Putting Together the Puzzle of Ion Transfer in Single-Digit Carbon Nanotubes: Ab Initio Meets Mean-Field, *Nanoscale*, 14 (2022) 8677-8690

(10) M Stolov, O Keisar, Y Cohen, V Freger, Elucidating the Effect of Aliphatic Molecular Plugs on Ion-Rejecting Properties of Polyamide Membranes, *ACS Appl. Mat. Interfaces*, 14 (2022) 3335-13343

(11) ZY Xiao, CE Diesendruck, V Freger, DR Dekel, Electropolymerization of Anion-Conducting Polymer Films, *J. Electrochem. Soc*. 169 (2022) 064506

(12) M Zelner, M Stolov, T Tendler, P Jahn, M Ulbricht, V Freger, Elucidating ion transport mechanism in polyelectrolyte-complex membranes, *J. Membr. Sci.* (2022) 120757

Presentations in international meetings/Events

We delivered during 2021-2022 invited and contributed talks at several international meetings, 4 in-person and 4 via Zoom or other on-line platforms including ECS 2021, Euromembrane 2021, NAMS 2022, dedicated workshops on nanofluidics, nanofiltration, electrokinetics etc.

List of grants:

1. NSF-BSF Program in Materials Research, US Collaborators: A. Noy (LLNL, UC Merced). M. Wanunu (Northeastern U), on ion-selective CNT membranes US$210,000/3 years, extended to 2022
2. MOST-BMBF, Program on Water Research, with M. Ulbricht (U Duisburg-Essen) on mosaic polyelectrolyte membranes, 200,000 Euro/3 years, extended to 2022
3. NewSkin, EU Horizon 2020 Project 862100, (~40 partners) on novel coatings and memrbanes, 720,000 Euro/4 years (to Freger group)
4. US-Israel Center for cooperation in water and energy, BIRD Foundation, US$8000

Work planned within INREP to 2022-2023:

We will finalize optimization of Nafion-PVDF electrospun composites using new thermomechanical fusion process and perform comprehensive characterization with the ain to commence testing in a FC in collaboration with other INREP members.

We will extend approach to other materials, especially, preparation of AEM.

We will continue our modeling work on ion uptake, conductivity and ion-selectivity in Nafion and other materials.

David Eisenberg's group

Team members working on fuel-cell-related projects in 2021:

- Dr. Eliyahu Farber
- Dr. Siniya Mondal
- Dr. Karina Ioffe
- Dr. Yakov Yasman
- Tomer Burshtein
- Inbal Offen-Polak
- Shir Tabac
- Yair Shahaf
- Nicola M. Seraphim
- Noam Zyser

Research Topic/s:

1) Catalysts development for AEMFCs and AEM electrolyzers
2) Development of flow-enhancing supports for high-power electrochemical devices
3) Development of post-hydrogen fuels for AEMFCs
4) Development of ORR, HzOR, AOR catalysts

5) Development of hydrogen carriers (urea)

Ultimate Research Goals in the Framework of the IFCC:

1) Highly active PGM-free catalysts for AEMFCs and AEM electrolyzers
2) Tunable-porosity supports, matchable to any electrocatalytic sites and application

Relevant instrumentation in the Eisenberg lab:

1) RRDE systems
2) N_2 sorption (BET)
3) TGA-DSC-MS
4) Differential electrochemical MS, also connected to TGA-DSC
5) 8 furnaces for different atmospheres of catalyst preparation

Major Achievements for FY2021:

1) Discovery of a new method for increasing power during electrocatalysis by a novel pore-formation mechanism. It is based on phase-separation in polymers, leading to mesoporosity, and conserved by cross-linking during pyrolysis (Burshtein *et al.*, *Small* **2021**)
2) Discovery of the mechanism by which flow-enhancing pores form during pyrolysis of an electrocatalytic carbon, prepared in a cheap and sustainable fashion from simple metal-organic salts (Farber *et al.*, *Chem. Commun.* **2021**)
3) Development of method for enhancing the disorder of hydroxide-based electrocatalysts, thus enhancing their electronic conductivity and exposed surface area, leading to higher currents. (Chakrabarty *et al.*, *J. Solid-State Electrochem.* **2021**)
4) Development of testing method for separating useful and useless components of ORR and HzOR catalysts, based on multi-doped Fe–N–C materials (Burshtein *et al.*, *PCCP* **2021**)

Go/no-Go points:

1) n/a

Plans for FY 2022 (please relate to the US DOE benchmarks and goals):

1) Development of ultra-stable Fe-N-C electrocatalyst by co-doping
2) Improving mass-transfer and power by focusing on pore connectivity

Which components developed in your lab in recent years can be implemented in a fuel cell today (also include scale in size and weight when relevant):

1) Porous carbon supports, with variable-size porosity
2) Molecular Fe-N_x moieties, introduced by a variety of methods to any carbonaceous support

Relevant publications 2021:

1. S. Chakrabarty,[=] I. Offen-Polak,[=] T. Y. Burshtein, E. M. Farber, D. Eisenberg, "Urea oxidation electrocatalysis on nickel hydroxide: the role of disorder", ***J. Solid State Electrochem.,*** *25,* 159-171, **2021**.
2. S. Tabac, D. Eisenberg, "Pyrolyze this paper: can biomass become a source for precise carbon electrodes?", ***Curr. Opinion Electrochem,*** 100638, **2021**.
3. R. Uwayid, N. M. Seraphim, E. N. Guyes, **D. Eisenberg**, M. E. Suss, "Characterizing and mitigating the degradation of oxidized cathodes during capacitive deionization cycling", ***Carbon,*** *173,* 1105-1114, **2021**.
4. T. Y. Burshtein,[=] I. Agami,[=] M. Sananis, C. E. Diesendruck, D. Eisenberg, "Template-free formation of regular macroporosity in carbon materials made from a folded polymer precursor", ***Small,*** 2100712, **2021**.
5. T. Ben Uliel,[=] E. M. Farber,[=] H. Aviv, W. Stroek, M. Ferbinteanu, Y. R. Tischler, D. Eisenberg, "Combining polarized low-frequency Raman with XRD to identify directional structural motifs in a pyrolysis precursor", ***Chem. Commun,*** *57,* 7015-7018, **2021**.
6. T. Y. Burshtein, D. Aias, J. Wang, M. Sananis, E.M. Farber, O. Gazit, I. Grinberg, D. Eisenberg, "Fe–N–C Electrocatalysts in the Oxygen and Nitrogen Cycles in Alkaline Media: The Role of Iron Carbide", ***Phys. Chem. Chem. Phys,*** *23*, 26674-26679, **2021**.

Presentations at conferences 2021:

1. Invited talk. "Hydrazine Oxidation Electrocatalysis on Multi-Doped Nanostructured Carbons", Electrochemistry Meets Nanoscience 2021, IIT Mandi–Israel. 2021.
2. "Hydrazine Oxidation Electrocatalysis on Multi-Doped Carbons: Who Does What?", MRS Spring Meeting (ONLINE). 2021.
3. "Hydrazine Oxidation Electrocatalysis on Multi-Doped Carbons", 239th Meeting of the Electrochemical Society, (ONLINE). 2021.
4. "Alkaline Hydrazine Oxidation Electrocatalysis on Multi-Doped Carbons: Looking for the Active Site", 240th Meeting of the Electrochemical Society, (ONLINE). 2021.

Grants 2021:

2020–2024 **Pazy Foundation** (~200k NIS x 4y), co-PI Dr. Amir Weitz, Rafael "Fuel Cells based on Alternative Fuels"

2019–2023 **Israel Science Foundation** (250k NIS x 4y + 100k Infrastructure Grant), "Carbide-Carbon Electrocatalysts for Hydrazine Oxidation"

2020 **Young GIF (German-Israeli Foundation)** (22,000 euro), "Designing Flow in Electrocatalysts"

2019–2021 **Israel Ministry of Energy** (145k NIS x 3y),
"Electrocatalysis for Energy: Solving the Flow Challenge"

<u>Other activities:</u>

2021–present Head of the Organic and Inorganic Department, at the Schulich Faculty of Chemistry

2021 Guest Editor, Israel Journal of Chemistry, special issue on Electrochemistry

2019–present Israel Electrochemical Society, Member of Board of Directors & Treasurer

<u>Avner Rothschild's group</u>

<u>Avner Rothschild's group in 2021 (people related to INREP)</u>

Avner Rothschild	Prof
David Shay Ellis	PhD, Senior researcher
Elena Davydova	PhD, Senior researcher
Yifat Piekner	PhD student (graduated)
Anton Tsyganok	PhD student
Ziv Arzi	MSc student (graduated)
Noya Haik	MSc student (graduated)
Ilya Slobodkin	MSc student
Yosi Halper	MSc student

The group of Avner Rothschild made progress in the following areas during 2021:

1. We developed new methods to measure electrooptical losses in transition metal oxide photoelectrodes for photoelectrochemical water splitting.
2. We discovered that hematite (iron oxide) photoanodes for photoelectrochemical water splitting lose about half of the absorbed photons for localized d-d electronic transitions that do not generate electron-hole pairs, solving a half-century old enigma and revealing the cause of underperformance of hematite photoanodes.
3. We developed a unique system with high sensitivity and high accuracy for spectral quantum efficiency measurements of photoelectrochemical solar cells.
4. We discovered an unusual light-bias effect on the quantum efficiency spectrum of $BiVO_4$ photoanodes for photoelectrochemical water splitting.

5. We developed carbon cloth supported nickel (oxy)hydroxide electrodes for E-TAC water electrolysis with superior performance compared to electrodes on nickel foam substrates.

Collaborations

During 2021 we maintained vital collaborations with H_2Pro
Within INREP we have strong collaboration Gidi Grader.
In addition, we have collaborations with Prof. Roel van de Krol (Solar Fuels Institute, HZB), Dr. Arik Yochelis (BGU) and Dr. Daniel Grave (BGU).

Publications in 2021 (related to the INREP activities):

1.) A. Landman, S. Hadash, A. Ben-Azaryah, G. E. Shter, H. Dotan, A. Rothschild and G. S. Grader, *High performance core/shell Ni/Ni(OH)$_2$ electrospun nanofiber anodes for decoupled water splitting*, **Advanced Functional Materials** 31, 2008118 (2021).

2.) D. A. Grave, D. S. Ellis, Y. Piekner, M. Kölbach, H. Dotan, A. Kay, P. Schnell, R. van de Krol, F. F. Abdi, D. Friedrich and A. Rothschild, *Extraction of mobile charge carrier photogeneration yield spectrum of ultrathin-film metal oxide photoanodes for solar water splitting*, **Nature Materials** 20, 833–840 (2021).

3.) Y. Piekner, D. S. Ellis, D. A. Grave, A. Tsyganok and A. Rothschild, *Wasted photons: Photogeneration yield and charge carrier collection efficiency of hematite photoanodes for photoelectrochemical water splitting,* **Energy & Environmental Science** 14, 4584-4598 (2021).

4.) D. S. Ellis, Y. Piekner, D. A. Grave, P. Schnell and A. Rothschild, *Considerations for the Accurate Measurement of Incident Photon to Current Efficiency in Photoelectrochemical Cells*, **Frontiers in Energy Research** 9, 726069 (2021).

Book chapters in 2021 (related to the INREP activities):

1.) A. Landman, A. Rothschild and G. Grader, New electrolyzer principles: Decoupled water splitting, in: Hydrogen Production by Water Electrolysis, edited by T. Smolinka and J. Gärche (Elsevier, 2021).

Patents granted in 2021 (related to the INREP activities):

1.) G. Grader, G. Shter, H. Dotan, A. Rothschild and A. Landman, System and method for generation of gases, United States Patent Application 2021/0017654 A1 (2021). (Licensed to H2Pro)

Special Achievements of the group during 2021:

1. Avner Rothschild and Gidi Grader received the Groundbreaking Research Prize, of the Eric and Sheila Samson Prime Minister's Prize for Global Innovation in Smart Mobility and Alternative Fuels for Transportation.

2. Avner Rothschild and Gidi Grader received the Guy Sella Research Prize in Energy.

3. Avner Rothschild was nominated a Fellow of the Royal Society of Chemistry.

4. Ziv Arzi graduated with a MSc thesis with distinction (Cum Lauda).

5. Noya Haik graduated with a MSc thesis with distinction (Cum Lauda).

6. Yifat Piekner received the Best Paper award of the Jacobs Graduate School (Technion).

7. Avner Rothschild was ranked by research.com among the Top Materials Science Scientists (#44 in Israel and #8046 in the world).

List of grants:

1. Industrial grants (during 2021): H2Pro 50K USD p.a..
2. Israel Science Foundation (ISF) grants: A new ISF grant was won in 2021 (together with Prof. Arik Yochelis from BGU), 1780K NIS (5 years).
3. Ministry of Science & Technology (MOST) grants: A new MOST grant was won in 2021, together with Gidi Grader (Technion, INREP), 636K NIS (2 years).

Work planned to 2022-2023:

We will continue to work on advanced electrodes for E-TAC water electrolysis; understanding capacity-rate limitation of nickel (oxy)hydroxide electrodes for rechargeable alkaline batteries, and developing a new process for decoupled water electrolysis.

Gideon Grader's group

Gideon Grader's group in 2020-22 (people related to INREP)

Gideon Grader	Prof
Gennady Shter	PhD, Senior researcher
Meirav Mann-Lahav	PhD, Senior researcher
Avigail Landman	PhD student (graduated)
Manar Halabi	MSc student (graduated)
Shabi Hadash	MSc student (graduated)
Yaniv Farkash	MSc student

The group of Gideon Grader made progress in the following areas during 2020-22:

1. We developed new methods to nickel nanofibers with controlled cross section and large surface area.

2. We developed methods to create ion-conducting nanofibers by electrospinning and tested their performance
3. We developed nickel fiber supported nickel (oxy)hydroxide electrodes for E-TAC water electrolysis with superior performance compared to electrodes on nickel foam substrates.

Collaborations

During 2020-22 we maintained vital collaborations with H_2Pro

Within INREP we have strong collaboration Avner Rothschild, as well as with Dario Dekel, Yair Ein-Eli and David Cahen.

Outside INREP, we have collaborations with Prof. Uri Banin, Roie Yerushalmi and David Avnir (HUJI), Oz Gazit (Technion).

Publications in 2021 (related to the INREP activities):

1.) Manar Halabi, Meirav Mann-Lahav, Gennady E. Shter, Oren Elishav, Gideon S. Grader and Dario R. Dekel, "Effect of humidity during electrospinning on the water uptake and conductivity of ionomer fibers", Polymer, **Vol. 12**, (2020) .

2.) Avigail Landman, Rawan Halabi, Paula Dias, Hen Dotan, Alex Mehlmann, Gennady E. Shter, Manar Halabi, Omayer Naserladeen, Adélio Mendes, Gideon S. Grader and Avner Rothschild, "Decoupled Photoelectrochemical Water Splitting System for Centralized Hydrogen Production", Joule, **4**, 448–471, (2020).

3.) N. Ralbag, E. S. Davydova, M. Mann-Lahav, P. Cong, J. He, A. M. Beale, G. S. Grader, D. Avnir and D. R. Dekel, "Ceria entrapped Palladium Novel Composites for Hydrogen Oxidation Reaction in Alkaline Medium", the Journal of The Electrochemical Society, **167**, 054514, (2020).

4.) A. Landman, S. Hadash, A. Ben-Azaryah, G. E. Shter, H. Dotan, A. Rothschild and G. S. Grader, "High performance core/shell Ni/Ni(OH)2 electrospun nanofiber anodes for decoupled water splitting", Advanced Functional Materials, **31**, 2008118 (2021).

5.) Dina Pinsky, Noam Ralbag, Ramesh Kumar, Singh, Meirav, Mann-Lahav, Gennady E. Shter, Dario R. Dekel, Gideon S. Grader and David Avnir, "Metal Nanoparticles Entrapped in Metal Matrices", Nanoscale Advances, RSC, 3, 4597 (2021).

6.) M Mann-Lahav, M Halabi, GE Shter, V Beilin, M Balaish, Y Ein-Eli, Dario R. Dekel, Gideon S. Grader , "Electrospun ionomeric fibers with anion conducting properties", Advanced Functional Materials, **30** (18), 1901733 (2021).

Book chapters in 2021 (related to the INREP activities):

1.) A. Landman, A. Rothschild and G. Grader, New electrolyzer principles: Decoupled water splitting, in: Hydrogen Production by Water Electrolysis, edited by T. Smolinka and J. Gärche (Elsevier, 2021).

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Special Achievements of the group during 2020-22:

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2. Avner Rothschild and Gidi Grader received the Guy Sella Research Prize in Energy.

3. Avner Rothschild and Gidi Grader received the RSC-2022 Horizon Prize Research.

4. Avner Rothschild and Gidi Grader received the Guy Sella Research Prize in Energy.

5. Shabi Hadash graduated with an MSc thesis.

6. Manar Halabi graduated with an MSc thesis.

List of grants:

1. Industrial grants (during 2021): H2Pro 50K USD p.a.
2. Ministry of Science & Technology (MOST) grants: A new MOST grant was won in 2021, together with Gidi Grader (Technion, INREP), 636K NIS (2 years).

Work planned to 2022-2023:

We will continue to work on advanced electrodes for E-TAC water electrolysis, and developing a new process for decoupled water electrolysis based on moving electrodes.

Matthew Suss' group

Current Team Members

First Name	Last Name
Robert	Gloukhovski
Amit	Shocron
Arunchander	Asokan
Prakash	Rewatkar
Ankita	Mathur
Rana	Uwayid
Jintao	Wu
Shada	Abu Khalla
Salman	Abdalla

Eilon	Miara
Zohar	Sahray
Anat	Wisenbrod
Mohamad	Aasarthen

Research Topic/s:

1) Novel redox flow batteries for grid energy storage applications
2) Porous electrode theory and material design for high power density
3) Electrocatalytic electrodes
4) Continuum theory of electrochemical systems (electric double layers, transport, etc)
5) Hybrid energy storage/water purification electrochemical systems

Relevant Instrumentation in your lab:

1) RRDE system
2) Rheometer
3) Several flow battery test stations
4) Supercapacitor test stations
5) Potentiostats for fundamental electrochemical experiments
6) Rapid prototyping equipment (CNC mill, laser cutter)
7) Tube furnace for electrode synthesis
8) glovebox, walk-in chemical fumehood

Major Achievements for FY2021:

1) Developed novel single-flow multiphase flow battery, enabling low-cost energy storage. Featured as a cover article in ChemSusChem journal.
2) Led a collaboration with MIT to establish the theoretical underpinning of multiphase flow batteries with a publication in 2020 in Electrochimica Acta.
3) Established a direct titration methodology to diagnose and study carbon electrode degradation, using advanced electric double layer models to interpret data and published in the journal Carbon.
4) Developed a novel fuel cell which simultaneously cleans water and produces electricity, which we termed the "desalination fuel cell", and demonstrated up to 96% thermodynamics energy efficiency.
5) Established a membraneless hydrogen-bromine redox flow battery with ultra-high power density (> 1 W/cm^2)
6) Developed microporous carbon electrodes which can be highly selective for specific ions, enabling novel electrochemical separations and published in the Proceedings of the National Academy of Sciences (PNAS).
7) Featured in the RSC "Emerging Investigator" series.

Go/no-Go points:

1) n/a

Plans for FY 2021 (please relate to the US DOE bench marks and goals):

1) Optimize the single-flow, multiphase flow battery for high Coulombic efficiency
2) Achieve 1.5 W/cm^2 power density for our membraneless hydrogen bromine battery
3) Develop scaling rules for the desalination fuel cell, and develop non-noble metal catalysts for this device
4) Improve the energy efficiency of our electrochemical selective separations system.

Relevant Publications FY2021:

1) R Uwayid, N Seraphim, EN Guyes, D Eisenberg, ME Suss. “Characterizing and mitigating the degradation of oxidized cathodes during capacitive deionization cycling.” Carbon, 173, 1105-1114, 2021.
2) L Amit, D Naar, R Gloukhovski, GJ la O’, ME Suss. “A single flow battery with multiphase flow.” ChemSusChem, 14, 991-991, 2021.
3) EN Guyes, A Shocron, Y Chen, C Diesendruck, ME Suss. “Long-lasting, monovalent selective capacitive deionization electrodes.” NPJ Clean Water, 4, 1-11, 2021.
4) JG Gamaethiralalage, K Singh, S Sahin, J Yoon, M Elimelech, ME Suss, P Liang, PM Biesheuvel, RL Zornitta, LCPM de Smet, “Recent advances in ion selectivity with capacitive deionization”, Energy & Environmental Science, 14, 1095-1120, 2021.
5) R Ronen, A Gat, MZ Bazant, ME Suss, “Single flow multiphase flow battery: theory.” Electrochimica Acta, 389, 138554, 2021.
6) F Yang, Y He, L Rosentsvit, ME Suss, X Zhang, T Gao, P Liang, “Flow-electrode capacitive deionization: a review and new perspectives.”, Water Research, 117222, 2021.
7) A Shocron, E Guyes, HHM Rijnaarts, PM Biesheuvel, ME Suss, J Dykstra. “Electrochemical removal of amphoteric species.” Proceedings of the National Academy of Sciences, 118, e2108240118, 2021.
8) Salman Abdalla, Shada Abu Khalla, ME Suss, “Voltage loss breakdown in desalination fuel cells.” Electrochemistry Communications, 132, 107136, 2021.
9) S Abu Khalla, I Atlas, S Litster, ME Suss. “Desalination fuel cells with high thermodynamic energy efficiency.” Environmental Science & Technology, 56, 1413-1421, 2022.
10) R Uwayid, E Guyes, A Shocron, J Gilron, M Elimelech, ME Suss, “Perfect divalent cation selectivity with capacitive deionization.” Water Research, 210, 2022.
11) ME Suss, Y Zhang, I Atlas, Y Gendel, EB Ruck, V Presser, “Emerging hydrogen-driven electrochemical water purification technologies”, Invited mini review, Electrochemistry Communications, 107211, 2022.
12) P Rewatkar, D Nath, PS Kumar, ME Suss, and S Goel. "Internet of Things enabled environmental condition monitoring driven by laser ablated reduced graphene oxide based Al-air fuel cell." Journal of Power Sources, 521, 2022.
13) A Asokan, S Abu Khalla, S Abdalla, ME Suss, “Chloride-tolerant, inexpensive Fe/N/C catalysts exceed platinum catalysts for desalination fuel cell cathodes”, Accepted & in press, ACS Applied Energy Materials, 2022.

14) I Atlas, J Wu, AN Shocron, ME Suss, "Spatial variations of pH in electrodialysis stacks: theory", Accepted & in press, Electrochimica Acta, 2022.
15) Uwayid R, Guyes EN, Shocron AN, Gilron J, Elimelech M, Suss ME. Perfect divalent cation selectivity with capacitive deionization. Water Research. 2022 Feb 15;210:117959.
16) Suss ME, Zhang Y, Atlas I, Gendel Y, Ruck EB, Presser V. Emerging, hydrogen-driven electrochemical water purification. Electrochemistry Communications. 2022 Mar 1;136:107211.
17) Ronen R, Gloukhovski R, Suss ME. Single-flow multiphase flow batteries: Experiments. Journal of Power Sources. 2022 Aug 30;540:231567.
18) Shocron AN, Atlas I, Suss ME. Predicting ion selectivity in water purification by capacitive deionization: electric double layer models. Current Opinion in Colloid & Interface Science. 2022 Jun 23:101602.
19) Uwayid R, Diesendruck CE, Suss ME. Emerging investigator series: a comparison of strong and weak-acid functionalized carbon electrodes in capacitive deionization. Environmental Science: Water Research & Technology. 2022;8(5):949-56.
20) Abdalla S, Khalla SA, Suss ME. Scaling Up the Simultaneous Production of Clean Electricity and Clean Water. Journal of The Electrochemical Society. 2022 Jun 10;169(6):063508.
21) Kuperman S, Ronen R, Matia Y, Zigelman A, Suss ME, Gat AD. Modelling the fluid mechanics in single-flow batteries with an adjacent channel for improved reactant transport. Flow. 2022;2.

Selected Presentations at Conferences 2021 (only international keynotes and invited talks listed)

1) ME Suss. "Numerical modeling unlocks remarkable ion selectivity of capacitive deionization", **Keynote Lecture**, 32nd topical meeting of the International Society of Electrochemistry, May 15-19th 2022, Aachen, Germany.
2) ME Suss. "Co-generation of electricity and desalted water using chemical energy." **Keynote Lecture**, 12th European Symposium on Electrochemical Engineering (ESEE), Leeuwarden, Netherlands, June 14th 2020 (postponed to June 2021 due to pandemic).
3) 2. ME Suss. "Remarkable ion selectivity by capacitive deionization with porous carbon electrodes" **Plenary Lecture**, 2021 Capacitive Deionization & Electrosorption Conference (CDI&E), May 11th 2021, Atlanta, USA (delivered remotely due to pandemic).
4) ME Suss. "Selective ion storage in capacitively charged nanopore electric double layers." **Invited Lecture**, 14th International Symposium on Electrokinetics (ELKIN 2021), Haifa, Israel, June 2021 (delayed to June 2022 due to pandemic)
5) ME Suss. "Desalination fuel cells." **Invited Lecture**, 240th meeting of the Electrochemical Society, Orlando, FL, USA, October 11-14, 2021.

Grants 2021:

2019-2021	A desalination fuel cell	Israel Innovation Authority (Kamin)	750k ILS	Matthew Suss
2019-2022	Development of breakthrough high energy density grid-scale storage battery	Bilateral Industrial Research & Devel. Fund (BIRD)	670k USD (215k USD	Matthew Suss, Primus Power
2020-2023	Membrane-free low cost high density redox flow battery (MELODY)	EU H2020-LC-BAT-2019 875524	4 M EUR (326k EUR	Coordinator: TU Delft, NL
2020-2023	Inhibition of dendritic growth on planar electrodes in flow batteries	Israeli Ministry of Energy (45/2019)	0.76 M ILS (0.34 M ILS	Matthew Suss, Ofer Manor
2020-2021	High performance metal-halide flow batteries	MIT International Sci. & Tech. Initiatives (MISTI) seed fund	30k USD	Matthew Suss, Martin Bazant
2020-2022	Collaborative Water-Energy Research Center (CoWERC)	Bilateral Industrial Research & Devel. Fund (BIRD)	~44k USD	Coordinators: Ben Gurion University & Northwestern University, USA
2021-2024	A low-cost single flow battery Leveraging multiphase flow	Israel Science Foundation (ISF)	1.2 M ILS	Matthew Suss
2022-2024	Ion selective capacitive deionization for the food industry	Israel Innovation Authority(IIA), Nofar	1.4 M ILS	Matthew Suss Charles Diesendruck Tnuva

Other activities:

2021-present: Associate Editor, Royal Society of Chemistry (RSC), Energy Advances

2016- present: Guest editor for various journals (Electrochimica Acta, Desalination, Journal of Physics Condensed Matter)

2015-present: delegate member, representing Israel in the European Federation of Chemical Engineering (EFCE), Working Group of Electrochemical Engineering.

2014-present: member (2014-present) & Chair (2015-2019): the International Working Group for Capacitive Deionization and Electrosorption

Summary of work

The Cleantech Innovations Laboratory led by Prof. Matthew Suss is affiliated with Mechanical Engineering, Chemical Engineering and the Grand Technion Energy Program at Technion. The lab has four major projects involving developing various novel and impact electrochemical systems: 1) a single-flow multiphase flow battery, 2) a membraneless high power density hydrogen-bromine battery, 3) desalination fuel cells, 4) ion selective capacitive deionization.

The group has an extensive track record of combining fundamental theory work and experimental work to achieve breakthrough device performance. Several of the world records and discoveries of the past 2 years: 1) Highest power density for a membraneless electrochemical cell (> 1 W/cm^2), 2) Highest cycle life for a capacitive deionization cell (1000 cycles), 3) Highest thermodynamic energy efficiency for chemically-driven water purification cells, 4) First working flow battery based on a single emulsive electrolyte, 5) first demonstration of perfect divalent cation selectivity in a CDI cell.

Ariel University

Alex Schechter's group

Hanan	Teller	PhD, Senior researcher
Daniel	Herranz	PostDoc
Parthiban	Velayutham	PostDoc
Anjali	*Kaiprathu*	PostDoc
Medhanie	Gebru	PhD student
Annie	Cleetus	PhD student
Radhey	Shyam Yadav	PhD student
Lea	Ouakanin	PhD student
Merin	Mary	Visiting PhD
Shilpa	Santosh	Visiting PhD

The group of Alex Schechter made progress in the following areas during 2021:

ORR Durability/Activity

- Exploring bi-functional ORR/OER catalyst made of Nickel iron spinel on exposed MoS2 surfaces for regenerative fuel cells and metal-air batteries.
- CeO_2 enclosed by N-doped carbon, derived from porphyrin polymers, provides onsite scavenging of peroxides formed during oxygen reduction at the cathode
- New Pt-free βAg2Se exhibit high ORR activity and stability in alkaline conditions as well as spinel nickel ferrite on MoS2 as bifunctional ORR/OER catalysts for regenerative FCs.

Hydrogen carrying fuels Catalysis

- Develop new catalysts for urea oxidation based on non-noble metals based on oxides or molecular organo-metallic complexes

- Understanding the instability mechanism of ammonia oxidation on the copper-based catalyst in alkaline electrolytes
- Develop low Pt anode catalysts loading for DME, Methyl formate methanol and their mixture in high power direct gas-fed fuel cells. Elucidation of the reaction mechanism steps of these anodic reactions using DFT and selected sector-electrochemical methods.
- Energy storage - Studying the reduction of N2 to ammonia on selected synthesized catalysts materials and various electrolytes.

Collaborations

During 2021 we maintained vital collaborations with the following industries:

4. NTC-WBU (Czech Republic)
5. Few groups from MGU (India)
6. A new collaboration with Dr. Charlotte Vogt from the Technion
7. Within INREP we have collaborations now with Daniel Nessim (BIU), Brian Rozen (TAU)
8. Other collaborations: DFT calculations of catalyst surfaces (Haya Kornweitz) Microbial fuel cells (Rivka Cahan (AU)), Anion exchange membranes (Flavio Grynszpan (AU)), and compact hydrogen reactors from borohydrides (Idit Avrahami (AU)

Publications in 2021 (related to the INREP activities):

1. System, device and method for hydrogen production, A Schechter, I Avrahami, US Patent App. 17/292,439

2. Edge Cooling of a Fuel Cell during Aerial Missions by Ambient Air, L Zakhvatkin, A Schechter, E Buri, I Avrahami, Micromachines 12 (11), 1432

3. Dependable polysulfone based anion exchange membranes incorporating triazatriangulenium cations, J Thomas, B Francis, S Thomas, A Schechter, F Grynszpan, Solid State Ionics 370, 115731

4. Hydrogen production in a semi-single-chamber microbial electrolysis cell based on anode encapsulated in a dialysis bag, S Rozenfeld, B Gandu, LO Hirsch, I Dubrovin, A Schechter, R Cahan, International Journal of Energy Research 45 (13), 19074-19088

5. Selectively-permeable membrane, A Schechter, E Bormashenko, O Krichevski, US Patent 11,084,001

6. Advances in catalytic electrooxidation of urea: A review, RK Singh, K Rajavelu, M Montag, A Schechter, Energy Technology 9 (8), 2100017

7. Hydrogen Production on Demand by a Pump Controlled Hydrolysis of Granulated Sodium Borohydride, L Zakhvatkin, M Zolotih, Y Maurice, A Schechter, I Avrahami, Energy & Fuels 35 (14), 11507-11514
8. Bioinspired oxygen selective membrane for Zn–air batteries, Krichevski, RK Singh, E Bormashenko, Y Bormashenko, V Multanen, ...
   a. Journal of Materials Science 56 (15), 9382-9394
9. Facile and scalable ambient pressure chemical vapor deposition-assisted synthesis of layered silver selenide (β-Ag2Se) on Ag foil as a possible oxygen reduction catalyst in …, R Konar, S Das, E Teblum, A Modak, I Perelshtein, JJ Richter, electrochimica Acta 370, 137709
10. Metal–organic polymer-derived interconnected Fe–Ni alloy by carbon nanotubes as an advanced design of urea oxidation catalysts, A Modak, R Mohan, K Rajavelu, R Cahan, T Bendikov, A Schechter, ACS Applied Materials & Interfaces 13 (7), 8461-8473
11. Electrocatalysts, the preparation thereof, and using the same for ammonia synthesis, Schechter, M Revanasiddappa, V Goldshtein, A Karajic, US Patent App. 17/043,884
12. Plasma-modified FeGly/C as a Pt-free stable ORR electrocatalyst in an acid electrolyte, R Mohan, A Modak, A Schechter, ACS Applied Energy Materials 4 (1), 564-574
13. Surface modifications of carbon nanodots reveal the chemical source of their bright fluorescence, A Dutta, STY Trolles-Cavalcante, A Cleetus, V Marks, A Schechter, ...

Work planned for 2022-2023:

We will continue to work on materials (catalysts/membranes) for fuel cells, sustainable synthetic fuels (hydrogen, ammonia and Small organic molecules)

We will continue to explore new bifunctional catalysts or HER/ORR

Our large effort to develop catalysts for direct oxidation of DME/MF gases in PEMFC will continue. We have a world record in direct DME fuel cells and we plan to explore ways to further improve it. For example utilizing fuel gas mixtures (H2,DME, MF) from a CO_2 reduction reactor dealing with the selectivity issue of active catalysts

We will start exploring electrolytes for CO2 reduction in aqueous and non-aqueous

One of our main mission in recent years was the study of electrochemical ammonia formation for large-scale energy storage. In this respect, we have made significant progress in the rate and faradic efficiency utilizing our bi-functionality approach and some newly unpublished results on an alternative mechanism for NRR.

A complimentary study on direct electrochemical ammonia oxidation on non-PGM catalysts will continue. We will focus on reaction mechanisms and understanding the degradation process of transition metal alloys and oxides.

Ben Gurion University

Menny Shalom's group

Current Team Members working on FC related projects (not only in the framework of the IFCC):

First Name	Last Name
Michael	Volokh
Jonathan	Tzadikov
Jiawei	Xia
Adi	Azoulay
Liel	Abisdris
Ayelet	Tashakory
Biswajit	Mondal
Alagar Raja	Kottaichamy
Rotem	Geva
Gabriel	Mark
Tirza	Shmila

Research Topic/s:

1) Development of materials for batteries and fuel cells

Relevant Instrumentation in your lab:

1) Potentiostat (with RDE)
2) GC
3) TGA-MS
4) High-temperature furnaces
5) Optical spectroscopy
6) Ball mill

7) High-power tip-sonicator

Major Achievements for FY2021:

1) Development of heteroatom-containing carbon materials (for example sulfur)
2) Development of transition-metal-phosphorous based electrocatalysts in carbonaceous matrices
3) Development of transition-metal oxide- or hydroxide-containing electrocatalysts

Go/no-Go points:

n/a

Plans for FY 2022 (please relate to the US DOE benchmarks and goals):

1) Combining the developed materials in sodium-ion and lithium-ion batteries and as substrates for fuel cells catalysts.
2) Synthesis of new composites based on black phosphorus, other metal-phosphides, carbon, nitrogen, and sulfur.

Which components developed in your lab in recent years can be implemented in a fuel cell today (also include scale in size and weight when relevant):

1) Nitrogen-doped carbons
2) Carbon-sulfur materials
3) Transition-metals (Ni, Co, Fe, and Mn) embedded into heteroatom-modified carbon materials (heteroatoms include B, P, S, N, and O).

Relevant Publications 2021:

1) J. Tzadikov, R. Geva, A. Azoulay, M. Shalom*, Facile Synthesis of Carbon-Sulfur Scaffold with Transition-Metal Sulfides and Oxides as Efficient Electrocatalysts for Oxygen Evolution Reaction, *ChemCatChem*, 2021, 13, 17, 3749–3753.
2) B. Mondal, N. Karjule, C. Singh, R. Shimoni, M. Volokh, I. Hod, M. Shalom*, Unraveling the Mechanisms of Electrocatalytic Oxygenation and Dehydrogenation of Organic Molecules to Value-Added Chemicals Over a Ni-Fe Oxide Catalyst, *Adv. Energy Mater*., 2021, 11, 2101858, 2021.
3) R. Geva, N. R. Levy, J. Tzadikov, R. Cohen, M. Weitman, L. Xing, L. Abisdris, J. Barrio, J. Xia, M. Volokh, Y. Ein-Eli, M. Shalom*, Molten sate synthesis of nickel phosphides: mechanism and composition-activity correlation for electrochemical applications, *J. Mater. Chem. A*, 2021, 9, 27629–27638.
4) S. Ghosh, B. Mondal, R. Shubasis, M. Shalom*, M. Bar Sadan*, Alcohol oxidation with high efficiency and selectivity by nickel phosphide phases, *J. Mater. Chem. A*, 2022, 10, 8238–8244.

Presentations at Conferences 2021:

n/a

Grants 2021:

A member in Minerva center grant number 117873.

2019–2021: Israel-China personal ISF–NSFC grant carbon-nitride polymer films incorporating heteroatoms for photo(electro)catalysis ($100k/year; Funding: Israeli Science Foundation (ISF)). PI: Menny Shalom.

2020–2025: European Research Council Horizon 2020 Starting Grant, MFreePEC – controlled growth of lightweight metal-free materials for photoelectrochemical cells, Grant Agreement No. 849068 (€299k/year; Funding ERC; PI: Menny Shalom)

2021–2023: Pazy Foundation grant "Design and Synthesis of Advanced Catalytic Materials Based on Carbon-Nitride for Solar Fuel Production and Pollutant Degradation

(124k NIS/year; Funding: Pazy Foundation). PI: Menny Shalom (BGU).

Collaborations inside INREP:

- Yair Ein-Eli
- Lior Elbaz
- Malachi Noked
- Dario Dekel

Summary of work

After establishing the use of molten-state intermediates to incorporate various heteroatoms as boron, nitrogen, and sulfur in a carbonaceous matrices as the final materials, we have expanded this approach to form interactions between metal cations and polycyclic aromatic hydrocarbons (PAH). Specifically, we have used this approach to form metal oxides and metal sulfides in a carbon-sulfur matrix for the oxygen evolution reaction (Figure 1). Pyrene and sulfur monomers that melt before the condensation are used. In the resulting molten-state intermediate, the metallic cations coordinate to Pyr and S. Subsequent heating affords the final

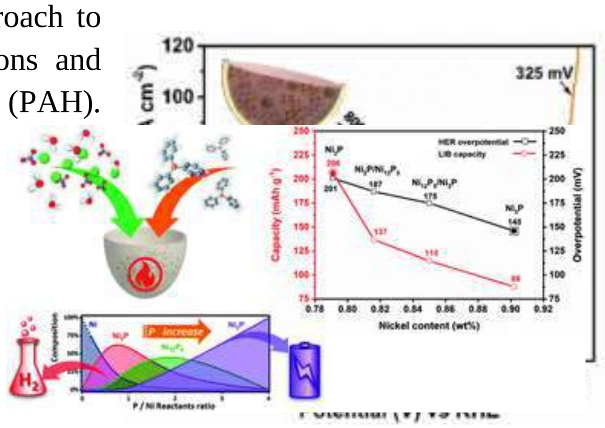

Figure 1: OER for CS matrix with metal oxides and metal sulfides

Figure 2: Ni materials for batteries and HER

materials, the elemental composition of which is controlled by varying the metallic amount used in the synthesis. The materials exhibit state-of-the-art activity as OER electrocatalysts in alkaline media, with overpotentials of 284 and 325 mV at current densities of 10 and 100 mA cm^{-2}. Elucidation of the electrochemical performance and the structural properties of the new materials reveal that the presence of carbon leads to smaller particles, resulting in a very high mass activity.

Nickel phosphides are highly attractive low-cost (electro)catalysts, thanks to their unique electronic structure, versatile phase diagram, and chemical stability. We have developed a single-step, simple, and scalable synthesis of nickel phosphides, with good control over phase composition, size, and catalytic activity, by a direct thermal reaction of nickel nitrate hexahydrate and triphenylphosphine (PPh_3) as shown in Figure 2. Upon heating, nickel ions are dissolved and coordinated by PPh_3, enabling the synthesis of fine-tuned particles, with nickel phosphide phases ranging from Ni_3P to Ni_2P. The strong metal–ligand complexation of Ni^{2+} with the P-center of PPh_3, with a ligand-to-metal charge transfer, produces a dominant P–Ni–P intermediate state, which suppresses highly toxic PH_3 release. Furthermore, the relative stability of the preferred intermediate state promotes the cleavage of P–phenyl bonds, releasing condensable aromatic by-products. In this reaction mechanism, PPh_3 serves both as P-source and as oxidants' scavenger, released as $OPPh_3$ when in excess. Ni_3P has the highest intrinsic electrocatalytic activity towards HER and high stability in acidic media, while Ni_2P is favorable for LIB anode materials, with the highest capacity and long-term cycling stability at high currents. The measured electrochemical activity is mainly dominated by the key factors of Ni/P ratio (*i.e.*, phase composition), particle size, carbon matrix presence (contributing to morphology and chemical stabilization, and enhanced electric conductivity). This new simple synthetic path offers new possibilities for the synthesis and design of low-cost catalytic materials with a wide variety of single and multi-component transition-metals.

We plan to use these materials alongside other transition metal phosphides, oxides, and sulfides for electrocatalytic reactions (*e.g.*, suitable for fuel cells, organic transformations) and for incorporation into batteries. For example, in 2021 we have published how nickel-iron oxyhydroxide formed from a metal-organic-framework allows the electrocatalytic selective oxidation of various alcohols (organic molecules upgrading) through oxygenation and dehydrogenation, with hydrogen coproduction. Detailed mechanistic studies unveil that C–H bond oxidation (with a bond dissociation energy $BDE_{C–H}$ of ≈88–96 kcal mol^{-1}) is involved in the rate-limiting step, which differs significantly from the oxygen evolution reaction mechanism. These findings show that the oxidation efficacy is linearly correlated with the $BDE_{C–H}$ of the molecule. Thus, the catalyst can be used as a general platform for large-scale electro-oxidation of various substrates through oxygenation and dehydrogenation at high current density (25 mA cm^{-2}), with a good Faradaic yield.

Hebrew University

Daniel Mandler’s group

First Name	Last Name
Netanel	Shpigel
Atanu	Roy
Mahdi	Azberga
Niv	Cohen

Research Topic/s:

1) Development of hybrid systems: battery-supercapacitors
2) Development of supercapacitors based on pseudocapcitive materials.
3) Development of MXene systems.
4) Studying Zn/electrolyte interface.
5) Studying S/electrolyte interface by scanning electrochemical microscopy (SECM).

Relevant Instrumentation in your lab:

1) Scanning electrochemical microscopy
2) Electrochemical QCM
3) FTIR
4) Lumisizer
5) Profilometer
6) Goniometer
7) UV-vis spectrophotometer

Major Achievements for FY2021 (please relate to the US DOE bench marks and goals):

1) Development of hybrid systems based on electrochemical and electrophoretic deposition.
2) Electrophoretic deposition of MXenes.
3) Electrophoretic deposition of MnO_2 as a pseudocapacitive materials.

Go/no-Go points:

n/a

Plans for FY 2022 (please relate to the US DOE bench marks and goals):

1) Start working on large scale bromine-based battery.
2) Demonstrate MXenes-based hybrid systems.
3) Improve the performance of hybrid systems.
4) Introduce the SECM for studying energy storage materials.

<u>Relevant Publications 2021:</u>

1. Yu, L. H.; Ong, S. J. H.; Liu, X. H.; Mandler, D.; Xu, Z. C. J., The importance of the dissolution of polysulfides in lithium-sulfur batteries and a perspective on high-energy electrolyte/cathode design. *Electrochimica Acta* **2021,** *392*, 6.

2. Wu, T. Z.; Ren, X.; Sun, Y. M.; Sun, S. N.; Xian, G. Y.; Scherer, G. G.; Fisher, A. C.; Mandler, D.; Ager, J. W.; Grimaud, A.; Wang, J. L.; Shen, C. M.; Yang, H. T.; Gracia, J.; Gao, H. J.; Xu, Z. C. J., Spin pinning effect to reconstructed oxyhydroxide layer on ferromagnetic oxides for enhanced water oxidation. *Nature Communications* **2021,** *12* (1), 11.

3. Noc, L.; Licen, M.; Olenik, I. D.; Chouhan, R. S.; Kovac, J.; Mandler, D.; Jerman, I., Polyhedral oligomeric silsesquioxanes as protective monolayer coatings against the high-temperature corrosion of concentrating solar power absorber surfaces. *Solar Energy Materials and Solar Cells* **2021,** *223*, 12.

4. Goei, R.; Ong, A. J.; Tan, J. H.; Loke, J. Y.; Lua, S. K.; Mandler, D.; Magdassi, S.; Tok, A. I. Y., Nd-Nb Co-doped SnO2/alpha-WO3 Electrochromic Materials: Enhanced Stability and Switching Properties. *ACS Omega* **2021,** *6* (40), 26251-26261.

5. Goei, R.; Ong, A. J.; Hao, T. J.; Yi, L. J.; Kuang, L. S.; Mandler, D.; Magdassi, S.; Tok, A. I. Y., Novel Nd-Mo co-doped SnO2/alpha-WO3 electrochromic materials (ECs) for enhanced smart window performance. *Ceram. Int.* **2021,** *47* (13), 18433-18442.

6. Deng, H. Q.; Peljo, P.; Huang, X. J.; Smirnov, E.; Sarkar, S.; Maye, S.; Girault, H. H.; Mandler, D., Ionosomes: Observation of Ionic Bilayer Water Clusters. *Journal of the American Chemical Society* **2021,** *143* (20), 7671-7680.

<u>Presentations at Conferences 2021:</u>

1) Invited lecture at the CEF Webinar Series, University of Southampton, Electrochemical Deposition: What's New since Faraday? May 13, 2021.
2) Invited lecture, Israelectrochemistry 2021, Beer Sheva, From Nano to Nano: Electrochemical Deposition using Nanomaterials as Building Blocks, June 8, 2021.
3) Invited lecture, ISEAC meeting 2021, Beijing (virtual). Nanoparticles Imprinted Matrices: A Method for the Selective Determination of Nanoparticles, August 25, 2021.
4) Plenary lecture at the 69^{th} ISE meeting in Korea, From Nano to Nano: Electrochemical Deposition using Nanomaterials as Building Blocks, August 31, 2021.
5) Keynote lecture at the 6th Ertl Symposium on Electrochemistry and Catalysis , November 26, 2020.
6) Forum of Nanopore Electrochemistry, Nanoparticles Imprinted Matrices: A Method for the Selective Determination of Nanoparticles, October 11, 2021.

Grants 2021 (only energy related projects):
2019-2021 Hebrew University-Academia Sinica (Taiwan) – Supercapacitors based on nanographene
2016-2021 Hebrew University-Nanyang Technological University (Singapore) - Nanomaterials for Energy and Water Research
2021-2023 China-Israel CNSF-ISF collaboration on hybrid systems for supercapacitors.

Other activities:
2019-present: Member of the Israel Electrochemical Society (ISEL) and representing the Israel section in the Electrochemical Society.

Summary of work

1. **Development of an electrochemical method for improving LiS batteries**: The dissolution of polysulfides is widely considered to be a major obstacle for developing lithium-sulfur batteries (LSBs) because it results in a shuttle effect. A popular strategy to address this issue is prevent- ing polysulfide dissolution, e.g., trapping/confining polysulfides in porous carbons. However, this conflicts with the advantage of commonly used ether-based electrolytes, i.e., the dissolution of polysulfides in such electrolytes is beneficial for delivering Li + to sulfur-based species compared to sluggish solid-state trans- port. Thus, a question is raised on the feasibility of the strategy to prevent polysulfide dissolution. Here, it is shown that the dissolution of polysulfides in ether-based electrolytes is necessary for a high capacity, suggesting that it might not be right to prevent the dissolution of polysulfides in such electrolytes. Thus, other approaches should be developed. A perspective is hence provided for designing electrolyte/cathode for high-energy LSBs.
2. **Novel electrochromic materials (ECs) for enhanced smart window performance**: In an urbanized city, about a third of total electrical consumption is allocated for indoor lighting and air conditioning system in residential and commercial buildings. The majority of the worldwide energy generation comes from burning of non-renewable fossil fuel which is not sustainable in the long run. The use of smart windows technology may catalyze the effort to reduce energy consumption of building and houses. More than 50% of heat entering a building through windows originate from the solar radiation in the near infrared (NIR) region. This candidate smart window material must exhibit dual-band (visible and NIR) modulation that allows selective modulation of NIR heat without affecting visible light transmission. A good electrochromic material in this respect should possess high visible light transmission, high NIR modulation, fast switching between colored and bleached state, and good stability over prolonged usage. In this work, we propose a novel Nd–Mo co-doped SnO_2/α-WO_3 electrochromic materials (ECs). As compared to the traditional SnO_2/α-WO_3 ECs, our Nd–Mo codoped SnO_2/α-WO_3 ECs exhibits up to 90% visible light transparency (at $\lambda = 600$ nm), 62% NIR modulation (at

wavelength 1200 nm), high coloration efficiency (~200 cm^2 C^{-1}), fast switching time with only 31% electrochromic performance drop (vs 59% of undoped sample) after up to 1000 reversible cyclic test. The enhanced electrochromic performance comes from the presence of Nd–Mo co-dopants that limit the trapping of Li^+ ion within α-WO_3 framework, reduce the extent of crystallization of α-WO_3 layer and enhancement of the electronic conductivity by transferring their excess electron to the conduction band of the SnO_2. To the best of the authors' knowledge, the present composition of ECs offers one of the better candidate materials for electrochromic to be used as thermal management layers on smart windows application.

3. **Hybrid energy storage systems**: Hybrid systems based on electrochemical deposition: Hybrid electric storage systems that combine capacitive and faradaic materials need to be well designed to benefit from the advantages of batteries and supercapacitors. The ultimate capacitive material is graphene, which offers high capacitance and conductivity. Yet, high capacitance is usually not achieved with graphite due to the restacking of its sheets. Therefore, an appealing approach to assembling high-energy, high-power hybrid graphene-based systems is to embed a faradaic 2D material in between the graphene sheets.

   We have developed a simple one-step approach along this line, whereby a faradaic material; layered double hydroxide (LDH), is electrochemically formed inside electrochemically exfoliated graphite. Specifically, graphite (GR) is exfoliated under negative potentials by Co(II) and in the presence of Mn(II) forms CoMn-LDH. The resulting GR-CoMn-LDH has a higher areal capacitance and energy density than similar hybrid supercapacitors due to the combination of capacitive and faradic type materials. The high areal capacitance is attributed to the exfoliation of the graphite at very negative potentials to form a 3D foam-like structure driven by hydrogen evolution as well as the deposition of CoMn-LDH due to hydroxide ion generation inside the graphite sheets. The ratio between the Co(II) and Mn(II) in the CoMn-LDH was optimized and the GR-CoMn-LDH was analyzed, and its electrochemical performance was studied. Analysis of a cross-section of the GR-CoMn-LDH confirmed the deposition of LDH inside the GR layers. The areal capacitance of the electrode was 186 mF cm^{-2} at a scan rate of 2 mV s^{-1}. Finally, an asymmetric supercapacitor (ASC) was assembled with GR-CoMn-LDH, and exfoliated graphite as the positive and negative electrodes, respectively, yielding an energy density of 96.1 μWh cm^{-3} and a power density of 5 mW cm^{-3}.

4. **Electrophoretic deposition of Mxene**: This 2D material was successfully dispersed and electrophoretically deposited by adding Ni^{2+} ions to the dispersion of the Mxene. The Ni^{2+} reversed the charge of the nanosheets of MXene and made it possible to deposit it under negative potentials. The mechanism of charging and deposition was studied and optimized. The different parameters, such as time and potential of deposition as well as the concentration and the nature of the metallic ions were also examined.

Daniel Sharon's group

Current Team Members working on polymer electrolyte and metal batteries:

First Name	Last Name
Omer	Blueman
Netta	Bruchiel SpanieR

Research Topic/s:

1) Development of solid-state polymer electrolytes
2) Development of rechargeable metal batteries

Relevant Instrumentation in your lab:

1) Probe-station for thin film measurements
2) Ellipsometer
3) ALD
4) Battery cyclers

Major Achievements for FY2021:

4) Development of block polymer and polymer blend electrolytes for Li batteries.
5) Development of new methods to visualize dendritic growth in metal batteries.

Go/no-Go points:

n/a

Plans for FY 2022 (please relate to the US DOE bench marks and goals):

1) Development of rechargeable Zn-metal batteries with polymer electrolytes.
2) Suppression of Li dendrite growth using nanostructured solid electrolytes.
3) Development of new synthetic methods for preparation of composite polymer electrolytes.

Relevant Publications FY2021

1. Akella, S. H.; Taragin, S.; Wang, Y.; Aviv, H.; Kozen, A. C.; Zysler, M.; Wang, L.; **Sharon, D**.; Lee, S. B.; Noked, M. Improvement of the Electrochemical Performance of LiNi 0.8 Co 0.1 Mn 0.1 O 2 via Atomic Layer Deposition of Lithium-Rich Zirconium Phosphate Coatings. *ACS Appl. Mater. Interfaces* **2021**.

2. Dykes, H.; R**.; Sharon, D**.; Noked, M.; Capraz, O. O. In Situ Stress Measurements on Thin Film Au Positive Electrode during the First Discharge of Li-O2 Batteries. J. Electrochem. Soc. **2021**.

3. Maddegalla, A.; Mukherjee, A.; Blázquez, J. A.; Azaceta, E.; Leonet, O.; Mainar, A. R.; Kovalevsky, A.; **Sharon, D**.; Martin, J. F.; Sotta, D.; Ein-Eli, Y.; Aurbach, D.; Noked, M. AZ31 Magnesium Alloy Foils as Thin Anodes for Rechargeable Magnesium Batteries. *ChemSusChem* **2021**.

4. Attias, R.; **Sharon, D**.; Goffer, Y.; Aurbach, D. Critical Review on the Unique Interactions and Electroanalytical Challenges Related to Cathodes - Solutions Interfaces in Non-Aqueous Mg Battery Prototypes. *ChemElectroChem* **2021**, *8* (17), 3229–3238.

5. Akella, S. H.; Taragin, S.; Mukherjee, A.; Lidor-Shalev, O.; Aviv, H.; Zysler, M.; **Sharon, D**.; Noked, M. Tailoring Nickel-Rich LiNi 0.8 Co 0.1 Mn 0.1 O 2 Layered Oxide Cathode Materials with Metal Sulfides (M 2 S:M = Li, Na) for Improved Electrochemical Properties . *J. Electrochem. Soc.* **2021**, *168* (8), 080543.

6. Chakrabarty, S.; Blázquez, J. A.; Sharabani, T.; Maddegalla, A.; Leonet, O.; Urdampilleta, I.; **Sharon, D.**; Noked, M.; Mukherjee, A. Stability of Current Collectors Against Corrosion in APC Electrolyte for Rechargeable Mg Battery. *J. Electrochem. Soc.* **2021**, *168* (8), 080526.

7. Deng, C.; Webb, M. A.; Bennington, P.; **Sharon, D.**; Nealey, P. F.; Patel, S. N.; De Pablo, J. J. Role of Molecular Architecture on Ion Transport in Ethylene Oxide-Based Polymer Electrolytes. *Macromolecules* **2021**, *54* (5), 2266–2276. [IF 5.985; Q1]

8. Bennington, P.; Deng, C**.; Sharon, D**.; Webb, M. A.; de Pablo, J. J.; Nealey, P. F.; Patel, S. N. Role of Solvation Site Segmental Dynamics on Ion Transport in Ethylene-Oxide Based Side-Chain Polymer Electrolytes. *J. Mater. Chem. A* **2021**, *9* (15), 9937–9951.

9. **Sharon, D**.; Bennington, P.; Dolejsi, M.; Webb, M. A.; de Pablo, J. J.; Patel, S. N.; Nealey, P. F. Molecular Level Differences in Ionic Solvation and Transport Behavior in Ethylene Oxide-Based Homopolymer and Block Copolymer Electrolytes. *J. Am. Chem. Soc.* **2021**, *143* (8), 3180–3190.

<u>Presentations at Conferences 2021:</u>

- Israel Electrochemical Society (ISEL), Ramat-Gan (2021) “Intrinsic properties of polymeric nanostructured solid electrolytes” (**invited**)

Grants 2021 (only energy related projects):

2021-2023: Research grant from the Ministry of Energy on the subject of "Development of organic-inorganic hybrid protection interfaces for rechargeable metal zinc batteries with long-term stability"

Summary of work

1. Development of solid-state polymer electrolytes: Solid-state batteries are regarded to be the most promising technology for unlocking the potential of energy storage applications in terms of both safety and energy density. Finding solid-state electrolytes with sufficient ionic conductivity, high interfacial stability and good mechanical properties is highly challenging. To address this challenge, our lab develops and studies multiphase organic (polymers), inorganic (ceramics), and hybrid solid-state electrolytes. We use electrochemical, microscopical and spectroscopical methods to characterize these materials before, during (*In-situ*) and after the cell operation (postmortem). These carefully designed materials and experiments allow us to explain the whole complicated behavior of the electrochemical system and logically change material attributes for optimal performance.
2. Development of rechargeable metal batteries: The introduction of solid-state electrolyte can unlock high energy technologies which are not safe and efficient enough in their liquid state. One of these systems is the Li-metal battery, where the anodic process is based on reversible deposition of Li metal. By using new materials systems and advance experiential platforms we are trying to develop new type of solid-state electrolytes (nanostructured electrolytes) that can stabilize metal electrodeposition and dissolution processes. If successful, we could potentially improve the safety and performance of Li/Na metal batteries.

Weizmann Institute of Science

Michal Leskes' group

Current Team Members working on battery related projects:

First Name	Last Name
Ayan	Maity
Isaac	Buchine
Asya	Svirinovsky Arbeli
Shira	Haber
Yuri	Shakhman
Shakked	Schwartz
Yuval	Steinberg
Ilana	Aksenfeld

Research Topic/s:

1) Ion transport across lithium and sodium metal SEI
2) Electrolytes dynamics and ion solvation
3) Surface chemistry of high voltage cathodes
4) Ion transport pathways, dendrite growth and degradation processes in composite electrolytes

Ultimate Research Goals in the Framework of INREP:

1) Correlate SEI composition and its ion transport properties
2) Develop composite electrolytes with improved conductivity and chemical stability
3) Identify main factors leading to efficient ionic transport across artificial coatings and develop efficient coatings for high energy cathodes and anodes.

Relevant Instrumentation in your lab:

1) 3 BioLogic cycling systems
2) 2 BioLogic portable cyclers connected to insitu NMR set ups.
3) Solid state NMR-DNP spectrometer
4) Benchtop EPR

Major Achievements for FY2021:

1) Developed a method to determine ion transport properties of the SEI formed on Li-metal and utilized it to compare the SEI formed in different electrolyte compositions
2) Developed a method to probe ion binding to the electrode surface
3) Identified decomposition pathways in composite electrolytes

Go/no-Go points:

n/a

Plans for FY 2022:

1) Determine the role of organic species in artificial coatings
2) Identify a protection layer for ceramic particles in composite electrolytes
3) Correlate SEI composition in difference electrolytes with electrochemical performance of anodes for Na battery cells.

Which components developed in your lab in recent years can be implemented in a battery today (also include scale in size and weight when relevant):

n/a

Relevant Publications 2021:

1. Haber, S, Rosy, Saha, A, Brontvein, O, Carmieli, R, Zohar, A, Noked, M & Leskes, M 2021, 'Structure and Functionality of an Alkylated LixSiyOz Interphase for High-Energy Cathodes from DNP-ssNMR Spectroscopy', Journal of the American Chemical Society, vol. 143, no. 12, pp. 4694-4704. https://doi.org/10.1021/jacs.1c00215

2. Jardón-Álvarez, D, Kahn, N, Houben, L & Leskes, M 2021, 'Oxygen Vacancy Distribution in Yttrium-Doped Ceria from 89Y–89Y Correlations via Dynamic Nuclear Polarization Solid-State NMR', Journal of Physical Chemistry Letters, vol. 12, no. 11, pp. 2964-2969. https://doi.org/10.1021/acs.jpclett.1c00221

3. Haber, S & Leskes, M 2022, 'Dynamic Nuclear Polarization in battery materials', Solid State Nuclear Magnetic Resonance, vol. 117, 101763. https://doi.org/10.1016/j.ssnmr.2021.101763

4. Jardón-Álvarez, D, Malka, T, van Tol, J, Feldman, Y, Carmieli, R & Leskes, M 2022, 'Monitoring electron spin fluctuations with paramagnetic relaxation enhancement', Journal of magnetic resonance (1997), vol. 336, 107143. https://doi.org/10.1016/j.jmr.2022.107143

5. Jardón-Álvarez, D & Leskes, M 2021, Dynamic nuclear polarization in inorganic solids from paramagnetic metal ion dopants. in Reference Module in Chemistry, Molecular Sciences and Chemical Engineering. Elsevier Inc. https://doi.org/10.1016/B978-0-12-823144-9.00027-3

Presentations at Conferences 2021:

1. Invited talk: Colloquium for Physical and Theoretical Chemistry, TUM, Germany (online)
2. Invited talk: Nano-seminars series, The Hebrew University, Jerusalem, Israel
3. Invited talk: International Conference on Hyperpolarization (Keynote), Lyon, France
4. Invited talk: IUPAC World Chemistry Congress 2021 (online)Plenary speaker: The 61st Rocky Mountain Conference on Magnetic Resonance, Colorado, USA - 07/2020 (postponed due to Covid-19)
5. Invited talk: EUROMAR, Slovenia (Virtual)

Grants 2021:

2020-2023: All Solid State Lithium-Ion Batteries with Controlled Interfaces: Champion Motors. PI: Malachi Noked, Michal Leskes.

2020-2023: Solution-Processable Recyclable Supercapacitors and Batteries: Champion Motors. PI: Boris Rybtchinski, Haim Weissman, Michal Leskes.

2020-2021: Deconstructing the Solid Electrolyte Interphase: Design Principles for Stable Lithium Battery Anodes from Solid-State NMR Spectroscopy

PI: Betar Gallant (MIT), Michal Leskes

2018-2023: Metal Ions DNP (ERC starting grant)

Other activities:

2020-present: Board Member of the Israel Electrochemical Society

Summary of work

Research in the Leskes lab is centered at developing and employing high sensitivity NMR based approaches for efficiently probing the bulk and interface of electrode and electrolyte materials. To this end we use solid state NMR as well as Dynamic Nuclear Polarization, a technique which provides sensitivity enhancement through transferring polarization from unpaired electrons introduced into the sample of interest.

In the past five years we have developed a new approach to increase NMR sensitivity in the bulk of inorganic materials by utilizing spin polarization transfer rom paramagnetic metal ion dopants. This approach provides atomic-molecular level chemical description as well as structural insight into the bulk and interface of materials. In 2021 we expanded the application range of this methodology extending it to solid electrolyte and other electrode materials. We have employed the approach to probe artificial coatings for high voltage cathodes as well as to probe the native SEI layer formed on titanates as anodes for Na ion batteries. Furthermore we introduced a new approach to gain high sensitivity at the surface of metallic anodes, this enables determining the chemical composition of the SEI formed on dendrites as well as the permeability of the SEI to ions.