

Thesis Changes Log

Name of Candidate: Nikita Akhmetov

PhD Program: Materials Science and Engineering

Title of Thesis: Development of Lithium-Conducting Polymer-Ceramic Membranes for Lithium-Metal Hybrid Flow Batteries

The thesis document includes the following changes in answer to the external review process.

The author would like to thank all the involved reviewers for their careful assessment, high appreciation, and fair criticism of the current Ph.D. thesis. Below, I have tried to carefully address the comments in a step-by-step manner.

The portions of the text inserted or modified in the Thesis document are *Italicized*.

Professor Evgeniy Antipov

Comment 1. p.113. What does it mean “we expect the changes in chemical composition” and “Li losses”? How the electroneutrality of the LATP’s crystal structure is achieved if the membrane fabrication takes place at low temperature?

Answer: According to our previous publications, LATP was proven to lose elements (including Li) and alter cell parameters during soaking in water. Hence, we expected similar behavior from LATP (both structural and elemental changes) in contact with the studied non-aqueous solvents used in membrane fabrication. In order to make these phrases more transparent, we rewrote the text on page 109 (the current page, after revision):

The fabrication led to the LATP’s cell shrinkage from 1304 to 1299-1300 Å³ for DMF- and DMSO-casted membranes (~0.38% loss). Moreover, the IC-sensitive [Li(1)O₆M₂] polyhedron diminishes from 16.0 to 15.6 Å³ (2.5% loss) for DMF and to 15.3 Å³ for DMSO and NMP (4.4% loss). The structural changes of the close extent were reported in our previous publication, where the impact of water was investigated [101,114]. In that work, these changes were accompanied with leaching the LATP elements out of the structure. Although we did not quantitatively estimate the elemental losses in the current study, we assume the presence of slight chemical degradation similar to that for the water case. Nevertheless, regardless of the solvent nature, XRD phase analysis showed no new crystallized compounds as well as depicted the maintenance of the initial NASICON phase of LATP.

Regarding the electroneutrality in LATP, it is always followed even during the membrane fabrication. If, for example, Li ions escape from the structure, Al compensates the loss, and the electroneutrality is restored.

Comment 2. p.115. Why so big discrepancy between experimental and theoretical values?

Answer: The most probable explanation is that the polymer matrix surrounding LATP particles can lower the precision of Al and Ti determination. On page 111, the values are averaged throughout the membrane surface. In ideal conditions, in the case of dense and polished ceramic, the element fractions correspond more to theoretical values.

Comment 3. P.134. Fig. 3.15. Why mean particle size of LATP is bigger for 60 min milling time compared to that one for 40 min milling time?

Answer: The mean particle sizes for 40- and 60-min milling times are close to each other and align within an error (instrumental + statistical). To clearly show it, Figure 3.15 (page 130) was modified accordingly by adding the error bars.

Comment 4. P. 197-199, Tables B1–B3. Wyckoff positions and standard deviations of coordinates and thermal parameters should be listed. What is the origin of the MO₆ volume variation?

Answer: The author appreciates the reviewer's commentary and added the Wyckoff positions and standard deviations to Tables B1–B3.

The origin of the MO₆ volume variation is likely connected with LATP composition changes. Particularly, the MO₆ polyhedra can get smaller when the Al/Ti ratio is reduced, as Al³⁺ is smaller than Ti⁴⁺. Another reason might be the depletion of Li in the neighboring polyhedra. In this case, oxygen is less attracted to the Li positions, gets closer to the Al/Ti site, and, hence, reduces the MO₆ volume.

Professor Yongdan Li

Comment 1. The LATP+PVDF is a good design, but the ionic conductivity should be still improved to facilitate the large-scale energy storage targets.

Answer: Indeed, the ionic conductivity of the modified LATP+PVDF membrane is not high enough and should be further improved. To stress its importance, the statement was revised (page 160, section 5.1):

Although we have broken the initial threshold for IC ($10^{-4} \text{ S cm}^{-1}$; 1.1, Table 5.1), it should be further increased to $10^{-3} \text{ S cm}^{-1}$ and higher to show the performance close to that of conventional LIBs. The further increase of the membrane's IC can be implemented by improving the inner interfaces through modifying the components, introducing linking and conductive agents, and developing alternative fabrication procedures.

Comment 2. The literature review part may be improved if a clearer description of the history of NARFB and the associated membrane is adopted.

Answer: The Literature review was modified according to this comment (pages 31, section 1.3.3):

Calling to the history of RFB development, P. Pissoort originally reported a vanadium redox couple in 1933 [39], while W. Kango first patented a titanium chloride flow cell in 1954 [40]. Thaller et al. began systematic investigations on Fe-Ti and Fe-Cr electrolytes in the 1970s as a part of NASA space missions [41,42]. At the start of the 1980s, an interest in electrochemical energy storage began to grow in Japan, where the Electrotechnical Lab developed Fe-Cr redox systems using hydrochloric acid [43]. A. Pelligri and P. Spaziante reintroduced the vanadium concept in 1978 [44], but a little progress was made. Later in 1986, Skyllas-Kazacos successfully demonstrated and commercialized an all-vanadium RFB [45,46]. Simultaneously, new technologies of vanadium mining and refining were developed (e.g., from soot of heavy fuels and titanium production) which boosted the interest in this metal. Such success stimulated an increase in vanadium RFB research resulting in the first commercial installations in the 2000s and shifting the Fe-Cr RFB technology from the scene. In recent years, a number of research groups and companies focus on improving existing cell design and developing new chemistries. Nowadays, vanadium RFBs are successfully tested for voltage sag compensation, emergency power supply, load levelling, power stability, etc.

In pages 36, section 1.3.3.1:

NAqRFBs were first described by Matsuda et al. in 1988 [59] and contained Ru-based active species dissolved in ACN. Besides noble metal complexes, in 2009 vanadium acetylacetonate was employed as an active component showing promising performance [60]. To resolve some of the organometallic compounds' issues (poor solubility, low stability), numerous organic molecules have been investigated as redox species since 2011 [61]. The resulting organic-based NAqRFBs operate at much higher cell voltages (up to 5-6 V), temperatures, and species concentrations that can theoretically increase RFBs energy and power density. At the same time, NAq solvents are more viscous than water, so one may expect lower IC.

Professor Atif Alzahrani

Comment 1. In Figure 4.1, the current density is stated as 0.1 mA/cm². It would be beneficial to clarify whether this same current density was applied for the redox flow battery cells. If not, it is recommended to include data for other (potentially higher) current densities.

Answer: Description for Figures 4.4 and 4.5 were modified according to the reviewer's suggestion to contain the applied current density.

Figure 4.4. Cycling performance of Li-TEMPO HFB cell operating with (a) 1.0 M LiClO₄ in PC, SE I; (b) 1.0 M LiClO₄ in EC:DEC, SE II; and (c) 1.0 M LiTFSI in EC:DEC, SE III; (d) Nyquist plots obtained for the Li-HFB cell before and after 100 cycles using SE III. Current — 0.5 mA, active area — 2.55 cm².

Figure 4.5. (a) Cell resistance before and after cycling tests of the Li-TEMPO flow cell operated with SE I–III. (b) Dependence of initial TCR on LiTFSI salt concentration in SE III–VI; (c) Discharge capacity and coulombic efficiency of the Li-TEMPO cell at 0.5 mA (2.55 cm² active area) using SE IV-based catholyte — 1 mM TEMPO + 0.75 M LiTFSI in EC:DEC; (d) Cell capacity retention times, t_{80} and t_{50} , of LATP+PVdF membranes fabricated via the original and modified routes.

Comment 2. Crossover is a significant concern in batteries, and in this thesis, it has been identified as the primary cause for capacity decay, which is highly plausible. Is there any direct evidence, such as characterizing the lithium side interface? Additionally, conducting a simple experiment to evaluate TEMPO crossover, such as using a two-compartment setup with one compartment containing pure PC and the other containing TEMPO/PC, could provide valuable insights. Monitoring the pure PC compartment over time could yield useful information.

Answer: Indeed, to evaluate the crossover of active species in the RFB cell, separate measurements of the membrane's permeability are essential. In my PhD thesis research, we utilized the sensitive voltammetry-based method to monitor TEMPO species transferring through the studied membranes. It has given a precise quantitative characterization of the membrane's permeability caused by concentration diffusion.

Monitoring in situ the TEMPO amount on the anode side of the real cell could be extremely useful, as we would be able to analyze charged species transferring owing to an electric field. However, such experiments require advancing the flow cell design, allowing for the analysis of the moieties with no losses during cell disassembly.

Comment 3. It would be helpful to understand how the ionic conductivities of the composite electrolyte were measured. Were any liquid electrolytes involved? If not, how does bare PVDF exhibit ionic conductivity, and what are the conductive ions involved?

Answer: The ionic conductivity of all the studied membranes was measured within coin cells equipped with stainless steel electrodes. All the samples were preliminarily soaked in lithium chlorate dissolved in propylene carbonate. For a more detailed description, one may refer to the respective experimental details in section 2.3.2 of the Thesis.

The pure polymeric (PVdF) membrane itself has a negligible ionic conductivity ($<10^{-6}$ S cm⁻¹) but a significant fracture of open porosity. Hence, in the case of soaking such a membrane prior to a coin cell assembly, the observed conductivity of $>10^{-5}$ S cm⁻¹ is likely dictated by the impact of the liquid electrolyte penetrated into the pore system.

Professor Albert Nasibulin

Comment 1. The list of figures and tables (p.16-22) is not necessary, and can be easily cut off without harming the quality of the thesis. This is old style, atavism.

Answer: The author appreciates the reviewer's suggestion. The lists of figures and tables were removed from the Thesis manuscript.

Comment 2. The thesis should start with short (2 page) Introduction showing the importance, revealing the challenges, and setting the goals for the thesis.

Answer: In accordance with the reviewer's commentary, the author inserted the 2-page Introduction section before the start of Chapter 1 (pages 16–17):

The need for energy storage reservoirs is anticipated to rise over the next few years due to the continuous transition to alternative energy producers. In excess of energy, the energy storage systems (ESSs) accumulate it and release it when there is a shortage. Redox flow batteries (RFBs) are ideal for stationary applications due to their independent scale of capacity and power, durability, and quick recharge by means of changing tanks with used electrolytes with ones that are charged. Despite the fact that water-based vanadium RFBs are the most developed kind, their widespread application is constrained by uneven vanadium availability, water instability, and low power density. As an alternative, RFBs based on non-aqueous (NAq) media provide higher operating voltages and greater redox chemistries' solubility. Moreover, NAqRFBs can convert the device into a hybrid flow battery (Li-HFB) by using low-potential metal anodes such as lithium. Such systems can combine the benefits of metal batteries (high energy density) and RFBs (scalability, extended cycle life). However, to boost Li-HFBs' performance and improve their applicability, a new ion-conducting, dense, and highly stable membrane should be developed. Besides the material design, one should simultaneously develop better manufacturing and characterization methods to make an acceptable membrane.

A potential direction to advance membranes is the creation of composite materials. The currently existing single-component solutions are unlikely to be suitable for Li-HFBs. Commercially available materials (Li-ion battery separators) possess large permeability, resulting in a high rate of active species crossover. Ion-exchange membranes, traditionally used in aqueous RFBs, show poor ionic conductivity (IC) and stability. Ceramics have a promising IC but remain unstable towards metallic lithium and/or air. The "filler-matrix", composite approach, combining the benefits of ceramic and polymer components, might generate a membrane product with potentially high IC, improved stability, flexibility, and integrity. To create the composite membrane appropriate for Li-HFBs, among the variety of materials we selected $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) NASICON-type ceramic and poly(vinylidene fluoride) (PVdF) polymer. With a solid structure, adequate electrochemical stability, and a promising IC ($>10^4 \text{ S cm}^{-1}$), LATP can be easily produced. The PVdF matrix, being simple to construct and handle, gives the system flexibility, improves its stability, and reduces crossover. To the best of our knowledge, no polymer-ceramic membranes for flow batteries have yet been suggested. Taking the prospect of the composite system for the Li-HFBs into consideration, we established the following **goal of the current Thesis**:

– to develop an ion-conductive, selective, and stable ceramic-in-polymer composite membrane for Li-metal hybrid flow batteries.

To accomplish this goal, a series of objectives based on the literature overview (Chapter 1) were further formulated in Section 1.7.

Comment 3. Chapter 5. Final Remarks is outside of the accepted structure of the thesis or should be properly named. Usually, the last section contains Conclusions and Future Perspectives (work).

Answer: The author has renamed the final chapter and subsections according to the reviewer's suggestion. Now, the structure is as following:

Chapter 5. Conclusions and Future Perspectives → *5.1. System Advances and Paths for Improvement;*
5.2 Conclusions of the Thesis.

Comment 4. Formulas and equations are part of the sentences and should follow the punctuation rules: commas and full periods are missing.

Answer: The author has corrected formula- and scheme-involved portions of text according to the reviewer's suggestion.

Also, the **abbreviation** of "ASSB" was moved to the origin of the list according to the alphabetical order.

Professor Stanislav Fedotov

Comment 1. While literature reports on LATP ceramic membranes show its instability against metallic lithium, why is the composite LATP+PVDF membrane found to be tolerant to it?

Answer: Indeed, the pure LATP ceramic material was reported to be unstable against metallic lithium, which leads to interface degradation and rapid failure of the cell. The idea behind the polymer introduction is to seal sensitive LATP particles into the stable PVdF matrix, which reduces direct contact between ceramic and Li metal. Of course, a complete isolation of LATP is barely possible, but we evidenced a high level of membrane stability by stripping/plating experiments (no failure, stable voltage amplitude), X-ray diffraction (no side phases, close cell parameters), SEM with energy-dispersive analysis, etc. No doubt, for a precise evaluation of the state of LATP and adjacent interfaces of the composite membrane, more powerful and comprehensive techniques are needed, such as XPS, neutron diffraction, AFM, and so on.

Comment 2. What contributes to the coulombic and energy efficiencies (CE and EE respectively) losses during the static cell operation? What are the CE and EE for the flow cell with TEMPO?

Answer: The observed coulombic efficiency (CE) decrease can be caused by multiple reasons that are hard to be exactly determined at such an early stage of research. However, in our case, the CE diminish might be associated with the slight degradation of the cell components, for instance, LATP or TEMPO active species. Of course, the exact reason should be more carefully evaluated in the future. Energy efficiency is more likely affected by the increase in ohmic losses or reduced species availability.

For the tested flow cell, CE was always at the level of 95-97%, which is comparable to that for the static cell. Although we did not calculate the EE for the flow one, we expected it to be lower (and less representative) owing to the larger volumes of catholyte utilized and the higher total cell resistance compared to the static cell.

Comment 3. Did you observe any corrosion of current collectors while using LiTFSI salt in the electrolyte?

Answer: In our study of cell performance, we used stainless steel as an anode current collector and graphite on the cathode side. Visually, we did not observe any degradation of these materials; however, an instrumental analysis of corrosion should be implemented in the future to ensure its absence.

Dr. Daniil Itkis

Comment 1. The authors says that the prepared membranes are stable in contact with metallic Li electrodes (in contrast to commercial samples of Nafion or Neosepta). This statement is based on impedance spectra analysis and analysis of bulk changes in the membrane (microscopy, XRD, etc.) Thus, the author connects the capacity fade of the battery prototypes just with crossover phenomenon. In my view, the interfacial stability should be analyzed more thoroughly. As far as I know, LATP is quite unstable towards reduction by metallic Li, PVDF-based systems also form interfacial films with Li. Additional stability in this work is gained by adding some supporting electrolyte (PC or EC:DMC based) onto the anode. Did the author tried to analyze what happens to the interface after cycling with some surface-sensitive tools? In addition to this, what about mechanical stability of the interface? Was any mechanical load applied to Li plate to ensure good contact with the membrane?

Answer: The author appreciates the reviewer's interest in the stability of membrane components to Li metal and the interfaces associated with them. Indeed, although the composite membranes showed bulk and interfacial stability, for deep understanding, more powerful, surface-sensitive tools such as AFM, XPS, etc. should be applied. We have not performed such analysis yet, but we plan to study the interfaces this way in the future.

Regarding the mechanical load, when assembling either a static or flow cell, we seal it with bolts and use rubber-based gaskets, so a tight contact is sufficient.

Comment 2. When the author writes about ionic conductivity, he often shows two-digit precision for the IC values. E.g., "Composite's IC diminished from $\sim 3 \cdot 10^{-4} \text{ S cm}^{-1}$ (for pure ceramic pellet) to 1.45, 1.04, and $1.70 \cdot 10^{-4} \text{ S cm}^{-1}$...". Can the author, please, comment on the precision of the measurement and on the reproducibility of these results (from point to point on one sample, from one sample to another, prepared in the same way).

Answer: The commentary from the reviewer regarding the precision is quite reasonable. To make the ionic conductivity representation clearer, we modified Figure 3.5 (page 112) to contain the respective error bar and updated the digit precision in the text (page 110, section 3.1.2):

Composite's IC diminished from $(3.1 \pm 0.5) \cdot 10^{-4} \text{ S cm}^{-1}$ (for pure ceramic pellet) to (1.45 ± 0.44) , (1.0 ± 0.3) , and $(1.7 \pm 0.5) \cdot 10^{-4} \text{ S cm}^{-1}$ for the same raw of the solvents (Figure 3.5) due to its in-matrix embedment and the slight impact of solvent.

Regarding the results reproducibility, the conductivity values within a single sample were quite close to each other and fell within the 5-% error. The value distribution for different samples within a single preparation was wider due to coin cell assembling features. Nevertheless, in general, it was possible to maintain a relative error of around 15%. In the particular case of Figure 3.5, the error was a bit higher owing to the smaller number of measurements than usual.

Comment 3. In the experimental part the author mentions that the membranes were prepared on the plasma-treated glass. What for the reason for treating the glass substrates with plasma? What type of plasma was used? How hard it was to detach the membranes from the substrate after drying?

Answer: The reason for treating the glass substrate is to improve its adhesion to the polymer solution by removing the organic contaminants and activating the surface. The treated substrate promotes homogeneous polymer distribution, uniform solvent evaporation, and a glossy morphology of the final membranes. At the same time, the membranes can be easily detached from the substrate after drying. The treatment was performed using air plasma at a low vacuum. To let a reader better understand the essence of the substrate treatment, we expanded the part in the Experimental section devoted to membrane fabrication (pages 90-91, section 2.2):

Commonly (except for several samples studied in the components mixing protocols part, Section 3.2.4), PVdF was firstly dissolved mixing at 400 rpm for 0.5 h at the temperature (T_{mix}) of 25–130 °C. Then, the rest composite components were added into the vial. The composite mixture was intensively stirred at 1400 rpm for 4 h with subsequent storing still for 20 h at RT for degassing. After that, the slurry was poured onto the specifically treated glass substrate. The treatment consistently includes: i) washing the glass with acetone; ii) drying the substrate with argon flow; iii) quenching the glass with air plasma at 0.2-0.3 atm. Such procedure

improves the substrate's adhesion with the polymer solution by removing the organic contaminants and activating its surface. The polymer slurry was then plated using the film applicator (Zehntner ZAA 2300, Switzerland) with the blade moved at 15 mm s^{-1} and the substrate temperature (T_{sub}) of $70\text{--}150 \text{ }^\circ\text{C}$. Finally, the samples were dried for 1 h at the drying temperature (T_{dry}) of $25\text{--}130 \text{ }^\circ\text{C}$ under various ambient pressure: atmospheric or dynamic vacuum.

Comment 4. The total cell resistances are given in absolute values, not normalized. I would prefer to have area normalized values as it makes easier to compare the results from different works.

Answer: The author accepts the reviewer's commentary regarding the representation of the total cell resistances. The descriptions for Figures 4.4 and 4.5 were accordingly modified and now contain the active area values for normalizing and comparing the resistances with literature data.

Figure 4.4. Cycling performance of Li-TEMPO HFB cell operating with (a) 1.0 M LiClO₄ in PC, SE I; (b) 1.0 M LiClO₄ in EC:DEC, SE II; and (c) 1.0 M LiTFSI in EC:DEC, SE III; (d) Nyquist plots obtained for the Li-HFB cell before and after 100 cycles using SE III. Current — 0.5 mA, active area — 2.55 cm².

Figure 4.5. (a) Cell resistance before and after cycling tests of the Li-TEMPO flow cell operated with SE I–III. (b) Dependence of initial TCR on LiTFSI salt concentration in SE III–VI; (c) Discharge capacity and coulombic efficiency of the Li-TEMPO cell at 0.5 mA (2.55 cm² active area) using SE IV-based catholyte — 1 mM TEMPO + 0.75 M LiTFSI in EC:DEC; (d) Cell capacity retention times, t_{80} and t_{50} , of LATP+PVdF membranes fabricated via the original and modified routes.

Comment 5. In my opinion, one of the most interesting fundamental results is the enrichment in fluorine concentration at the polymer-LATP interface after cycling. But in the thesis the discussion of this phenomenon is quite short. Can the author give more comments on this? What can be the mechanism for this? Can LiF be formed at the interface?

Answer: Indeed, the enrichment of LATP ceramic edges with fluorine is a very intriguing. As the polymer's fluorine unlikely bonds with LATP's oxygen, we preliminarily associate Li with being involved in the interface arrangement during cell cycling. We assume interfacial Li can participate in the ionic conductivity processes and be originated not only from the ceramic but also from liquid electrolyte or Li anode. Unfortunately, the analysis performed is insufficient yet to state so. At this moment we cannot explain the exact mechanism of the polymer-ceramic interface formation, so it should be further studied by more powerful techniques, for instance, tomography, AFM, XPS, and so on.