

# SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

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| <b>SCHOLAR NAME:</b>   | Sam Chen   |
| <b>FACULTY ADVISOR:</b>  | Jennifer L. Schaefer   |
| <b>PROJECT PERIOD:</b>   | May 22 to July 28, 2023  |
| <b>PROJECT TITLE:</b>  | Polymers in Next-generation Rechargeable Batteries   |
| <b>CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):</b> | <input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear<br><input checked="" type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar<br><input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind |

## MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

| RESEARCH GOALS   | ACTUAL PERFORMANCE AND ACCOMPLISHMENTS  | % OF GOAL COMPLETED |
|--|---|---------------------|
| <b>Investigate Li-ion transference</b>   | Electrochemical impedance spectroscopy results suggest high lithium-ion transference for perfluoropolyether tetra-acrylate (PFPEA) based GPE, but further study is needed to verify whether it's due to GPE or battery setup.             | 85                  |
| <b>Investigate oxidative stability of chosen gel-polymer electrolyte (GPE)</b> | Data from linear scan voltammetry suggests that PFPEA has high oxidative stability.   | 100                 |
| <b>Investigate discharge capacity of Li-ion battery containing chosen GPE.</b> | We found that lithium-ion battery containing PFPEA based GPE only discharges at low current rates, and it has low cathode utilization. However, the GPE preserves its discharge capacity after many cycles, which suggests its potential. | 80                  |
| <b>Investigate limiting current of Li-ion battery containing chosen GPE</b>    | PFPEA based GPEs become unstable when current density is above 0.1 mA/cm, suggesting material starts to dissociate.   | 100                 |

## RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

| CATEGORY   | INFORMATION  |
|--|--|
| <b>EXTERNAL PROPOSALS SUBMITTED</b>                                  | (Sponsor, Project Title, PIs, Submission Date, Proposal Amount)  |
| <b>EXTERNAL AWARDS RECEIVED</b>                                      | (Sponsor, Project Title, PIs, Award Date, Award Amount)  |
| <b>JOURNAL ARTICLES IN PROCESS OR PUBLISHED</b>                      | (Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)<br><br>Title: <b>In-situ Crosslinked Gel Polymer Electrolytes Based on Ionic Monomers for Lithium-Ion Batteries</b><br>Author: Peng He, <b>Sam Chen</b> , Yun Young Choi, Nosang V. Myung, and Jennifer L. Schaefer<br>Rest of the information is to be determined. |
| <b>BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH</b>                   | (Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)   |
| <b>PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH</b>             | Undergraduate Symposium Summer 2023, and Undergraduate 3MT competition, High transference gel polymer electrolyte in Li-ion battery, 07/26/2023, University of Notre Dame  |
| <b>AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT</b> | (Purpose, Title, Date Received)  |
| <b>INTERNAL COLLABORATIONS FOSTERED</b>                              | (Name, Organization, Purpose of Affiliation, and Frequency of Interactions )   |
| <b>EXTERNAL COLLABORATIONS FOSTERED</b>                              | (Name, Organization, Purpose of Affiliation, and Frequency of Interactions)  |
| <b>WEBSITE(S) FEATURING RESEARCH PROJECT</b>                         | (URL)  |
| <b>OTHER PRODUCTS AND SERVICES (e.g., media</b>                      | (Please describe each item in detail)  |

reports, databases, software, models,  
curricula, instruments, education programs,  
outreach for ND Energy and other groups)

### RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

**The experience was awesome. I work with Schaefer's lab group during the regular school year, and the summer research experience allowed me to participate in research full-time. The lab personnel are very helpful and friendly. To improve the experience even more, I think we should provide more social activities for the students during the summer.**

# FINAL WRITTEN REPORT

The primary focus of this summer research is studying the properties of perfluoropolyether tetra-acrylate (PFPEA) based gel polymer electrolyte. The electrolyte solvent is mixed ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate with a volume ratio of 3/3/4. The macromonomer is PFPEA, and the ionic monomer is lithium acrylate-propyl (trifluoromethane sulfonic) imide (LiAPTFSi). Compositions are labeled as macromonomer-ionic monomer-mass ratio-weight percent-solvent. For instance, the 10 wt.% GPE with a mass ratio of 2:1 macromonomer: ionic monomer is produced with 6.67 wt.% PFPEA, 3.33 wt.% LiAPTFSi, and 90 wt.% EC/EMC/DMC, ignoring the mass of the initiator. With research data from the previous school year, extensive testing was only done on 2 compositions of GPE: PFPEA-APTFSi-11-10 and PFPEA-APTFSi-21-10. Data collected for those two compositions include Li-ion transference, oxidative stability, battery discharge capacity, and limiting current result.

We determined our GPEs lithium-ion transference number using method proposed by Bruce, Vincent, and Evans. Figure 1 shows the polarization profile of PFPEA-APTFSi-11-10 and PFPEA-APTFSi-21-10 electrolyte, and Table 1 summarizes the Li<sup>+</sup> transference number and the parameter obtained from fitting the data to the equivalent electric circuit.

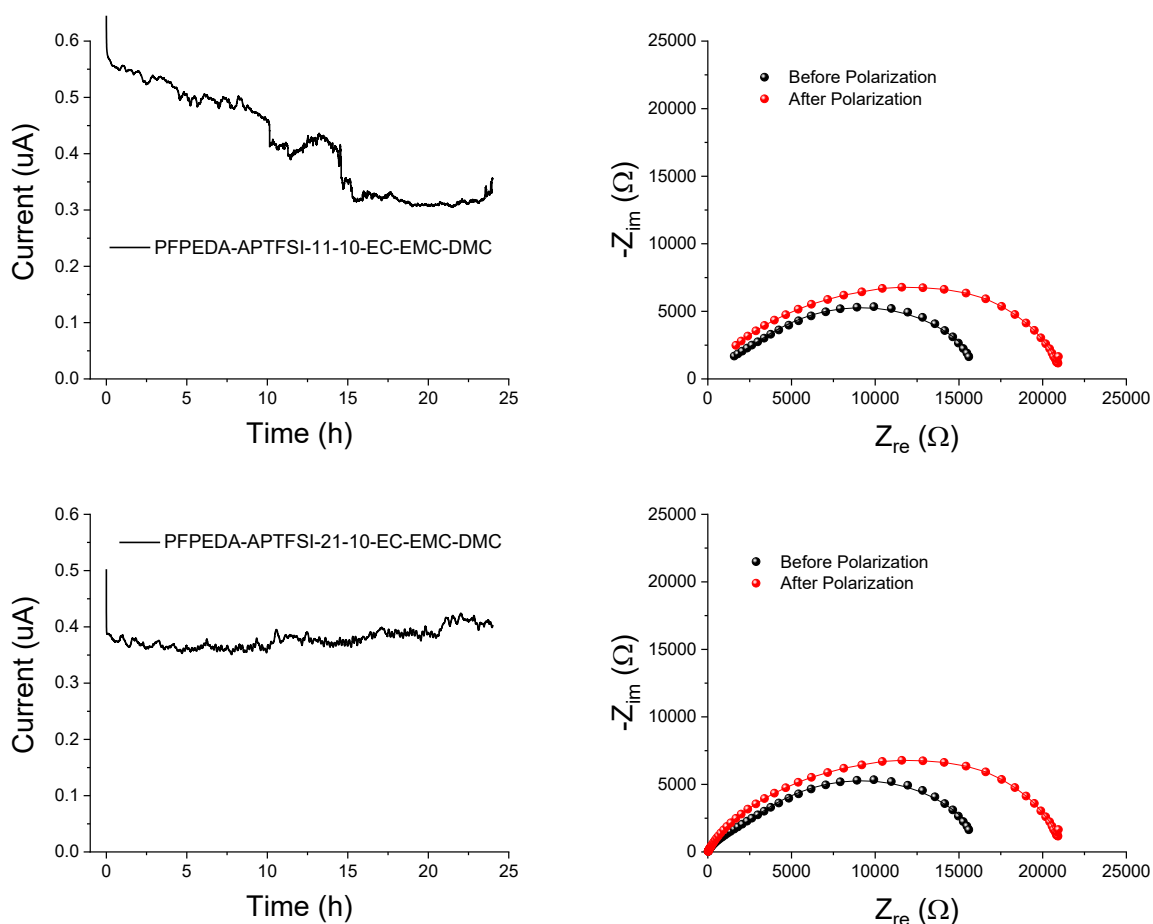


Figure 1. a) Polarization curve and b) EIS measurements for Li/PFPEA-APTFSi-11-10-EC-EMC-DMC/Li, d) Polarization curve and d) EIS measurements for Li/PFPEA-APTFSi-21-10-EC-EMC-DMC/Li.

Table 1. Currents and resistances of the two GPEs

| Sample                        | $i_0$ (uA) | $i_{ss}$ (uA) | $R_0$ ( $\Omega$ ) | $R_{ss}$ ( $\Omega$ ) | $t_{Li^+}$ |
|-------------------------------|------------|---------------|--------------------|-----------------------|------------|
| PFPEA-APTFSi-11-10-EC-EMC-DMC | 0.755      | 0.356         | 2045               | 6926                  | 0.532      |
| PFPEA-APTFSi-21-10-EC-EMC-DMC | 0.529      | 0.400         | 970                | 914                   | 0.744      |

The Li<sup>+</sup> transference numbers for both GPEs are high, indicating that the ionic monomer is crosslinked with macro monomer after polymerization and Li-ion is the primary conducting ion. However, the interfacial resistance is significantly higher than the bulk resistance, which may cause the modeled result to be inaccurate.

The oxidative stability of the GPEs is measured in size 2032-coin cells with an Li/GPE/Al cell configuration. The coin cell was assembled with an Al foil with an electro-spun PVDF mat placed in the bottom coin cell casing. 30  $\mu$ L of GPE monomer solution was added to the PVDF mat. Then, a Li foil disk was placed on the top of the PVDF mat as the working electrode. The Al/GPE/Li battery was then subjected to linear scan voltammetry (LSV) from 3 V to 6 V vs Li<sup>+</sup>/Li at a scan rate of 1 mV/s. GPEs were also tested with high-potential chronoamperometry. The cell configuration is the same as used for the LSV measurement. The cell was scanned from the potential as assembled to 5 V vs Li<sup>+</sup>/Li at 0.1 V increments. The cell was maintained at each potential for 2 h. The data collected is plotted in Figure 2 below.

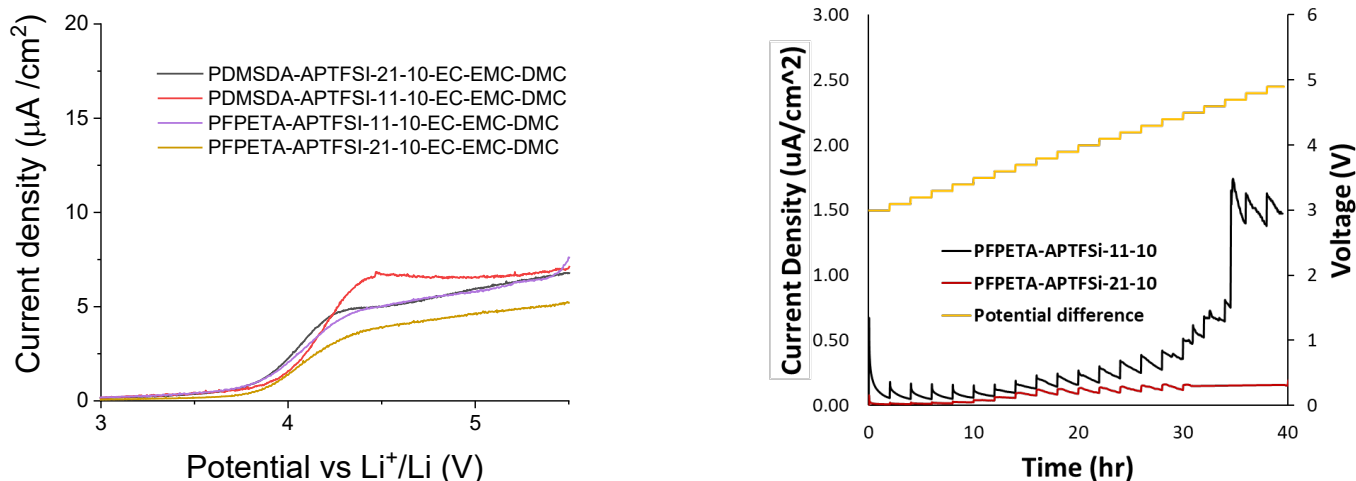


Figure 1. a) LSV measurements and b) High potential chronoamperometry of PFPETA-APTFSi-11-10 and PFPETA-APTFSi-21-10

Figure 2. a) includes previously collected data to provide a better comparison between different polymer based GPEs. Although it indicates an oxidative instability around 4.2V, the electrolytes appear to be stable with continued voltage increase up to 5.5 V. Figure 1. b) shows a similar result. The current densities of the two electrolytes appeared to be stable and remained low until the voltage increased above 4.5V.

The GPEs' discharge capacity is measured with graphite/NMC-811full cell configuration. Due to the failure of extracting useful information when cycling the cells at higher rates, an alternative method was designed to investigate the cells' performance. The cells are cycled at C/20, C/10, and C/5 for 10 cycles each. To further understand the electrochemistry and Li-ion transport limitation within the cell during the cycling process, the limiting current density of two samples is assessed in Li/Li symmetric cells. Those results are plotted in Figure 3 below.

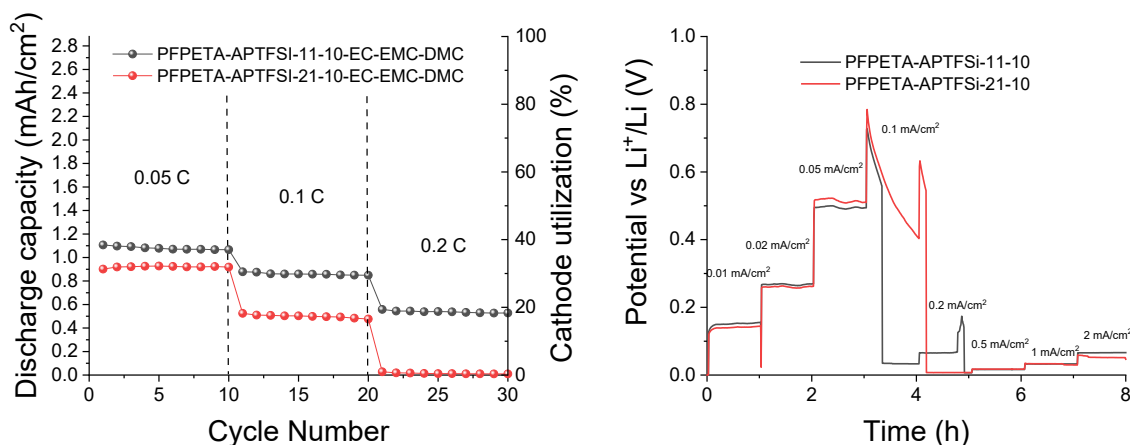


Figure 3. a) Rate performance and b) limiting current of PFPETA-APTFSi-11-10 and PFPETA-APTFSi-21-10

The cathode utilization for both PFPETA-based GPEs is around 40% at C/20 and drops drastically as cycling rates increase. It is far from ideal and can be resulted from the lack of ion permeation of the GPEs. However, the GPEs show good capacity retention and further research should be undertaken to improve the Li<sup>+</sup> transport phenomenon. To future investigate the lithium transport limitation, the limiting current density of two samples is assessed in Li/Li symmetric cells. Figure 2. B) suggests that the battery can be charged up to 0.05 mA/cm<sup>2</sup> before potential fluctuation happens. When current density increases above 0.05 mA/cm<sup>2</sup>, the sudden drop of potential profile suggests significant chemical activity occurred within the cells.