

# RESEARCH SYNOPSIS

Dipobrato Sarbapalli

(217) 979-1550 • [dipto032@gmail.com](mailto:dipto032@gmail.com) • [linkedin.com/in/dipto032/](https://www.linkedin.com/in/dipto032/) • [dipto032.github.io](https://github.com/dipto032)

**Summary.** I am trained as an experimental materials scientist, with skills in the domain of materials characterization on electrochemical energy storage systems and ceramic/cement-based binder materials. Additionally, I utilize techniques such as chemical vapor deposition, sol-gel synthesis, and steric entrapment for synthesizing carbon films and aluminosilicate materials relevant for my research. I also develop and maintain my own Python scripts for rapid data analysis and plotting.

My doctoral research focuses on correlating carbon structures with performance as electrodes for Li-ion, Na-ion and redox-flow batteries. Additionally, I have industry experience through an internship, where I worked on developing Li metal batteries with solid-state polymer electrolytes. My master's [thesis](#) focused on identifying nucleation mechanisms in novel aluminosilicate binders intended as a replacement for cement in construction applications. With the exposure to these classes of materials, I can apply my skills towards practical problems in batteries, ceramic and cement materials, which constitute some of the most vital technological systems in the modern world.

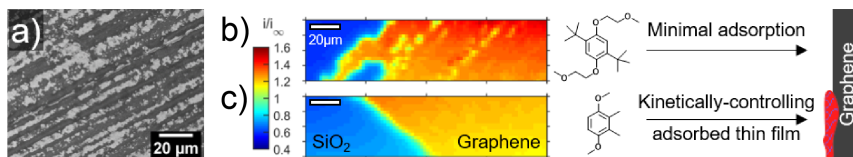
**Doctoral Research.** The 2019 Nobel Prize in Chemistry for the development of Li-ion batteries serves to highlight its impact on modern lifestyle. However, in the bigger picture, grand challenges exist in the development of electrochemical energy storage solutions for applications such as grid-level energy storage.[1] With current lithium reserves being insufficient for such a huge demand, additional low-cost and versatile battery technologies are needed, prepared with earth-abundant materials such as carbon.

*My doctoral research focuses on a two-pronged approach for i) developing analytical techniques and ii) tailoring interfaces on carbon materials, to advance the understanding of electrode-electrolyte interfaces in Li-ion and beyond Li-ion battery technologies.*

*a) Scanning Electrochemical Microscopy (SECM) for characterizing flow battery interfaces*

Non-aqueous redox flow batteries (nRFBs) are an upcoming candidate for grid-level storage applications,[1] with energy being stored by charging redox-active organic molecules (ROMs). These high-energy molecules can potentially take part in parasitic processes at the interface during (dis)charge, thereby decreasing the capacity and power capabilities of an nRFB. *My research led to the development of robust, widely applicable testing protocols with scanning electrochemical microscopy (SECM) to screen ROMs for parasitic reactions at electrode interfaces.*[2]

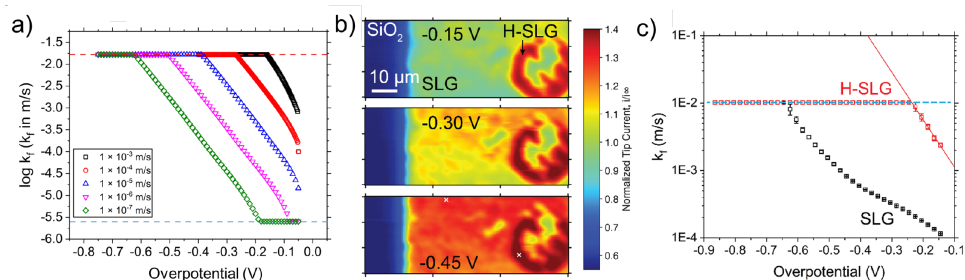
In brief, SECM is an electrochemical scanning probe measurement that can spatially resolve and quantify electron transfer (ET) rate constants between a ROM and an electrode.[3, 4] Our results on practically relevant ROMs revealed inhibition of ET owing to film formation on basal planes of graphene electrodes (**Fig. 1**). Edge planes of carbon appeared to be immune to these film formation processes, therefore providing powerful design guidelines for carbon electrode material selection in nRFBs.



**Figure 1:** SECM characterization of electron-transfer (ET) rates between graphene films and ROMs. a) SEM micrograph of graphene showing variation in layer numbers of graphene. b) and c) SECM measurements revealing spatial distribution in electrochemical reactivity, with color bar quantifying ET kinetics. The lack of heterogeneity in ET kinetics due to varying layer numbers of graphene in c) is attributed to the formation of films.[2]

Further improvements in this approach were made to reduce the testing time, and extract parameters quantifying ET kinetics. To this end, I have developed a SECM-based point measurement using COMSOL finite element simulations. The method is capable of rapidly evaluating ET kinetics ( $k_f$ ) between ROMs and any electrode material as a function of overpotential or polarization applied at the electrode (**Fig. 2a**).

Consequently, this approach enables comparison with theoretical kinetic models such as Butler-Volmer, to check for deviations from ideal ET processes at the interface. Using this SECM approach, I have characterized the role of carbon surface structure on ET kinetics. Single-layer graphene (SLG) electrodes were microfabricated to have areas with  $sp^3$  hybridized hydrogenated graphene (H-SLG) using  $H_2$  plasma. Ferrocene, an ideal ROM was observed to exhibit fast, ideal behavior over H-SLG, compared to pristine SLG, indicating molecular adsorption to be limiting ET kinetics (**Fig. 2b and 2c**). This phenomenon ties in closely to our previous observation of edge planes (likely functionalized and possessing  $sp^3$  hybridization) exhibiting no passivation in ET kinetics with practical ROMs for nRFBs.

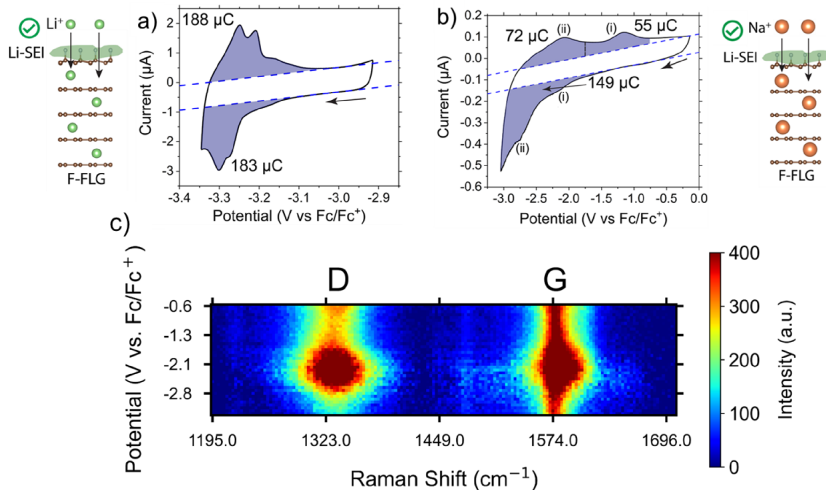


**Figure 2:** Quantifying ET behavior using COMSOL finite element simulations and experiments using SECM. a) Results from COMSOL simulations. b) SECM imaging revealing faster ET kinetics over H-SLG compared to SLG. c) SECM point measurement reveal ET kinetics to be conforming with Butler-Volmer model over H-SLG

*b) Tailoring anode electrolyte interfaces in alkali-ion batteries through surface functionalization*

Na-ion batteries are one of the promising and cheaper candidates in the realm of beyond Li-ion chemistries.[5] However, replacing Li with Na is challenging, with a major obstacle being the thermodynamic instability of  $Na^+$  intercalated graphite structures, among others. We hypothesized that these thermodynamic instabilities could be overturned by using 2D materials with distinct surface electronic properties that create favorable conditions for  $Na^+$  intercalation. As a solution to this problem, we recently presented theoretical calculations[6] which highlighted that a fluorine surface modifier built over

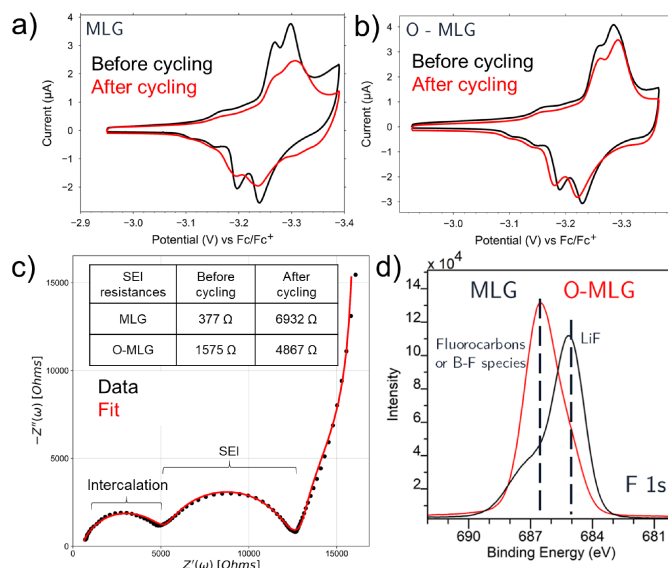
a thin, 4-layer graphene structure resulted in thermodynamically favorable  $Na^+$  intercalated graphene structures. Experimentally, using a combination of cyclic voltammetry (CV, **Fig. 3a, 3b**) and in-situ Raman spectroscopy (**Fig. 3c**), we were able to prove  $Na^+$  intercalation in these materials, with capacities  $\approx 10\times$  higher than previously reported in experimental literature.[7] A key finding from our experimental study was the identification that the native solid-electrolyte interphase (SEI) formed on graphite anodes posed a



**Figure 3:**  $Na^+$  intercalation in fluorinated few-layer graphene (F-FLG). a) Initial SEI formation and measurement of  $Li^+$  capacity in F-FLG using CV at a rate of 1 mV/s. b) Subsequent  $Na^+$  intercalation signature in the same sample at 1 mV/s. c) In-situ Raman data showing intercalation signature for dilute  $Na^+$  intercalation in F-FLG, as evidenced from D and G peak broadening, and small shifts in D peak position

barrier to  $\text{Na}^+$  intercalation. We circumvented this problem by performing a Li-based SEI by cycling F-FLG in Li-electrolyte solution, followed by cycling in Na-electrolyte solution to achieve  $\text{Na}^+$  intercalation. *These results highlight surface modification as a potential strategy for enabling charge storage in thermodynamically unfavorable systems.*

In addition to thermodynamic effects, we explored the effects of surface modification on the kinetics of  $\text{Li}^+$  intercalation processes, which in turn is heavily influenced by SEI formation. Surfaces of multi-layer graphene (MLG) were modified by exposure to reactive plasma sources such as  $\text{O}_2$  to yield O-MLG.  $\text{Li}^+$  intercalation was studied through CV and electrochemical impedance spectroscopy (EIS). CV measurements before and after cycling revealed greater deterioration in  $\text{Li}^+$  intercalation kinetics with MLG as compared to O-MLG anodes (**Fig. 4a, 4b**). A comprehensive EIS analysis accompanied by curve-fitting revealed that the sluggish kinetics were arising from  $\text{Li}^+$  transfer through the SEI (**Fig. 4c**). Ex-situ analysis using x-ray photoelectron spectroscopy (XPS) revealed significant differences in SEI chemical composition, notably in LiF content (**Fig. 4d**). *These observations illustrate that surface functionalization routes could be used to direct SEI formation, resulting in a robust and functional interphase for fast  $\text{Li}^+$  kinetics in graphitic carbon anodes.*



**Figure 4:**  $\text{Li}^+$  intercalation explored in surface modified MLG anodes). CV illustrating poor intercalation kinetics in a) MLG, compared to b) O-MLG anodes, as evident from peak splitting values. c) EIS data, and fit results revealing kinetic losses originating from mass transfer resistances across SEI. d) Ex-situ XPS of the SEI formed in MLG vs. O-MLG.

## References

- [1] Lynn Trahey et al. "Energy storage emerging: A perspective from the Joint Center for Energy Storage Research". *Proceedings of the National Academy of Sciences* 117.23 (2020), pp. 12550–12557. DOI: [10.1073/pnas.1821672117](https://doi.org/10.1073/pnas.1821672117).
- [2] Tylan S. Watkins, Dipobrato Sarbapalli, Michael J. Coughlan, Andrew S. Danis, Jingjing Zhang, Lu Zhang, Kevin R. Zavadil, and Joaquín Rodríguez-López. "A combined SECM and electrochemical AFM approach to probe interfacial processes affecting molecular reactivity at redox flow battery electrodes". *J. Mater. Chem. A* 8 (2020), pp. 15734–15745. DOI: [10.1039/D0TA00836B](https://doi.org/10.1039/D0TA00836B).
- [3] Michael J. Coughlan, Dipobrato Sarbapalli, and Joaquín Rodríguez-López. "The Chalkboard: Picture Your Electrode: A Primer on Scanning Electrochemical Microscopy". *Electrochemical Society Interface* 29.3 (2020), pp. 30–32. DOI: [10.1149/2.f03203if](https://doi.org/10.1149/2.f03203if).
- [4] Dipobrato Sarbapalli, Abhiroop Mishra, Kendrick O. Hatfield, Zachary T. Gossage, and Joaquín Rodríguez-López. "Scanning electrochemical microscopy: a versatile tool for inspecting the reactivity of battery electrodes". *Batteries*. 2053-2563. IOP Publishing, 2021, 9-1 to 9-44. DOI: [10.1088/978-0-7503-2682-7ch9](https://doi.org/10.1088/978-0-7503-2682-7ch9).
- [5] Michael D. Slater, Donghan Kim, Eungje Lee, and Christopher S. Johnson. "Sodium-Ion Batteries". *Advanced Functional Materials* 23.8 (2013), pp. 947–958. DOI: [10.1002/adfm.201200691](https://doi.org/10.1002/adfm.201200691).
- [6] A. Nijamudheen, Dipobrato Sarbapalli, Jingshu Hui, Joaquín Rodríguez-López, and Jose L. Mendoza-Cortes. "Impact of Surface Modification on the Lithium, Sodium, and Potassium Intercalation Efficiency and Capacity of Few-Layer Graphene Electrodes". *ACS Applied Materials & Interfaces* 12.17 (2020), pp. 19393–19401. DOI: [10.1021/acsami.9b23105](https://doi.org/10.1021/acsami.9b23105).
- [7] Dipobrato Sarbapalli et al. *Chem. Mater.*, Submitted (2022).