

COVER PAGE

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ACCOMPLISHMENTS

Organic radical polymers (ORPs) are rapidly growing in interest due to their unusual electronic nature and their wide breadth of potential applications. This is exemplified by the intense interest in organic radical batteries, which offer fast charging, high power, and excellent rate capability. Because it is an organic material, radical polymers can be potentially derived from biomass or other natural resources, and its availability is more secure than other electrode materials that are comprised of rare or toxic metals. Currently, the major challenges for organic radical batteries are (i) the low conductivity of the ORPs, (ii) a lack of a quantitative understanding of electron and ion transport, (iii) reconciling that understanding with conflicting results in the solid-state literature, and (iv) addressing swelling effects arising from favorable polymer-solvent interactions. Accordingly, there is a need to develop a fundamental understanding of the diffusion and kinetics of the redox reaction of organic radical polymers.

This proposed experimental project consisted of three objectives: Objective 1: Verify, Refine, and Harness the Diffusive Hopping with Segmental Mobility Model to Design High-Rate Organic Radical Polymers; Objective 2: Quantify Internal and External Ion Transport in Organic Radical Polymers; and Objective 3: Orchestrating and Understanding Internal Electron Transfer in Conjugated Radical Polymers.

This project led to many accomplishments, which we detail in chronological order to show how the accumulation of knowledge has benefited the research community.

1) Published November 2018 in *Nature Materials*, we showed for the first time a quantitative view of in situ ion transport and doping in organic radical polymers during the redox process. Specifically, two modes of both cation and anion exchange were shown, verifying that the solvent and its electrolyte play a role in charge storage. This was one of the first quantitative reports of electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) on mixed electron-ion-solvent transport in organic radical polymers.

2) Organic radical polymers face a challenge in their analysis in that they partially dissolve during cycling. Therefore, we demonstrated a thermally-activated crosslinking chemistry that simplified not only practical cycling but also practical EQCM-D analysis, published in *Chem Sus Chem* of January 2020. Since then, our group has widely adopted this chemistry in many other studies.

3) Published in August 2020 in *Chemical Science*, we demonstrated the phenomena of internal “self-discharge” using EQCM-D of conjugated radical polymers provided by Prof. Ober of Cornell. This finding taught that radical and conjugated backbone groups of different redox potentials can experience self-exchange.

4) Published in *Nature* May 2021, we reported the first-ever polypeptide organic radical batteries that could degrade on-command. The redox-active polypeptides were designed by Prof. Wooley. With support from this DOE project, we performed the electrochemical analysis of the organic radical polypeptides. It was shown that the battery could be degraded into amino acids and

byproducts at-will. This concept is a first step toward fully circular batteries that do not rely on metals. This work was later translated into the first-ever polypeptide organic radical redox flow battery, published in *Materials Advances* 2022.

5) In parallel, we began to turn our attention to metal-free aqueous organic radical batteries, which offer enhanced safety and reduced dissolution. Published in May 2021 in *Cell Reports Physical Science*, we identified the role of water-polymer interactions in determining the organic radical polymer's capacity and redox kinetics. Specifically, the polymer should have favorable water interactions (but not so favorable as to tend toward dissolution) such that electrolyte can slightly swell the electrode.

6) Published in February 2022, we examined the layer-by-layer formation and electrochemical performance of organic radical polyelectrolytes. We showed that the charged groups could act as self-doping agents. The polymers were provided by Prof. Regen.

7) Last, in a paper that is in revision for *Nature Materials*, we show why the energy storage of an organic radical polymer can vary by as much as 1000% by simply changing the electrolyte salt. Accomplished with EQCM-D, we show that this effect is due to swelling and ion-solvent interactions. Further, we report impedance spectroscopy coupled with EQCM-D for the first time to reveal the relative time scales of the reactions.

8) Two review articles were published during this period. The 2020 *ACS Macro Letters* review introduced the community to the general materials science and structure-property considerations of organic radical polymers. The 2022 *Journal of Polymer Science* review provided a practical guide for new users of QCMD to further broaden access.

9) Eight peer-reviewed research articles and two review articles were published in high-profile journal such as *Nature* and *Nature Materials*. One research article is in revision.

10) Public attention toward the projects findings occurred through the following outlets: the DOE Homepage, Nature PodCast, Chemical & Engineering News, Science Blog, Nature Asia, BBC Future, Tech Xplore, Mirage News, ScienMag, EurkeAlert!, New Atlas, Innovazione, Gizmag Emerging Technology Magazine, Device Materials Community, Next Big Future, La Stampa, La Repubblica, The Waire, Massive Science, World Economic Forum, Enerzine, Chem Europe, Science Daily.

11) Three graduate students and one post-doctoral researcher participated on the project. Three of these four participants are female. Two of the three graduate students have since graduated and are now doing post-docs within the US.

12) Results were presented at several conferences and institutions, including the Electrochemical Society meetings, the American Institute of Chemical Engineers meetings, American Chemical Society meetings, World Economic Forum Meeting of New Champions.

PUBLICATIONS

- 1) Wang S, Li F, Easley AD, Lutkenhaus JL. Real-time insight into the doping mechanism of redox-active organic radical polymers. *Nature Materials*. 2019;18(1):69-75. doi: 10.1038/s41563-018-0215-1.
- 2) Wang S, Park AMG, Flouda P, Easley AD, Li F, Ma T, Fuchs GD, Lutkenhaus JL. Solution-Processable Thermally Crosslinked Organic Radical Polymer Battery Cathodes. *ChemSusChem*. 2020;13(9):2371-8. doi: 10.1002/cssc.201903554.
- 3) Wang S, Easley AD, Thakur RM, Ma T, Yun J, Zhang Y, Ober CK, Lutkenhaus JL. Quantifying internal charge transfer and mixed ion-electron transfer in conjugated radical polymers. *Chemical Science*. 2020;11(36):9962-70. doi: 10.1039/D0SC03567J.
- 4) Wang S, Easley AD, Lutkenhaus JL. 100th Anniversary of Macromolecular Science Viewpoint: Fundamentals for the Future of Macromolecular Nitroxide Radicals. *ACS Macro Letters*. 2020;9(3):358-70. doi: 10.1021/acsmacrolett.0c00063.
- 5) Easley AD, Vukin LM, Flouda P, Howard DL, Pena JL, Lutkenhaus JL. Nitroxide Radical Polymer–Solvent Interactions and Solubility Parameter Determination. *Macromolecules*. 2020;53(18):7997-8008. doi: 10.1021/acs.macromol.0c01739.
- 6) Nguyen TP, Easley AD, Kang N, Khan S, Lim S-M, Rezenom YH, Wang S, Tran DK, Fan J, Letteri RA, He X, Su L, Yu C-H, Lutkenhaus JL, Wooley KL. Polypeptide organic radical batteries. *Nature*. 2021;593(7857):61-6. doi: 10.1038/s41586-021-03399-1
- 7) Ma, T, Easley, AD, Wang, S, Flouda, P, Lutkenhaus, JL. Mixed electron-ion-water transfer in macromolecular radicals for metal-free aqueous batteries. *Cell Reports Physical Science* 2021, 2 (5), 100414. doi: <https://doi.org/10.1016/j.xcrp.2021.100414>
- 8) Easley AD, Shaligram SV, Echols IJ, Nixon K, Regen SL, Lutkenhaus JL. Layer-by-Layer Nanoarchitectonics of Electrochemically Active Thin Films Comprised of Radical-Containing Polymers. *Journal of The Electrochemical Society*. 2022;169(2):020510. doi: 10.1149/1945-7111/ac4cd9.
- 9) Liang Z, Nguyen TP, Attanayake NH, Easley AD, Lutkenhaus JL, Wooley KL, Odom SA. Metal-free polypeptide redox flow batteries. *Materials Advances*. 2022;3(16):6558-65. doi: 10.1039/D2MA00498D.
- 10) Easley, AD, Ma, T, Eneh, CI, Yun, J, Thakur, RM, Lutkenhaus, JL. A practical guide to quartz crystal microbalance with dissipation monitoring of thin polymer films. *Journal of Polymer Science* 2022, 60(7), 1090. doi: <https://doi.org/10.1002/pol.20210324>
- 11) Ma T, Han C-H, Tabor D, Lutkenhaus JL. Uncovering the Origin of the Electrolyte’s Role in Metal-free, Aqueous Radical Batteries. *In Revision with Nature Materials*. 2022.

PEOPLE WORKING ON THE PROJECT

Shaoyang Wang - doctoral student at 50% effort. Wang conducted research on EQCM-D of organic radical polymers, crosslinkable radical polymers, and conjugated radical polymers, resulting in her papers in *Nature Materials*, *Chemical Science*, and *ChemSusChem*. Shaoyang is now in a post-doctoral researcher position.

Alexandra Easley – doctoral student support by an NSF Graduate Research Fellowship. She was supported 0% on this project but spent about 25% of her effort on this project. Easley examined the electrochemistry of organic polypeptide radicals and layer-by-layer assemblies of organic radical polymers resulting in papers in *Nature*, *Journal of the Electrochemical Society*, and *Macromolecules*. Easley is now in a post-doctoral researcher position.

Ratul Mitra Thakur – doctoral student at 50% effort. Ratul, a junior graduate student, assisted both Wang and Ma, and was in training for the next generation of this project.

Ting Ma – post-doctoral research at 75% effort. Ting examined metal-free aqueous electrolyte-organic radical polymer redox-chemistry, resulting in a paper in *Cell Reports Physical Science*. Ma continues on in the Lutkenhaus group.

Jodie Lutkenhaus – principal investigator at one month/year support, ~8% effort. Lutkenhaus oversaw the participant recruitment, execution of the project, experimental design, writing of papers, and reporting.

ESTIMATE OF THE UNEXPENDED FUNDS

\$3,449.01 remain as unexpended funds. This is less than 10% of the original budget.

