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Preventing Crossover in Redox Flow Batteries through Active Material Oligomerization

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Could the secret to better battery storage lie in linkage length?

The ability to store large quantities of energy generated by renewable, but intermittent, sources like solar or wind in systems integrated within the country's electrical grid is critical to the reduction of CO₂ emissions and slowing the rate of global warming. Among the energy storage technologies under consideration, redox flow batteries are promising candidates. While large-scale installations of vanadium-containing flow batteries have been utilized in Japan and China, the widespread adoption of these batteries for grid storage purposes has been limited due to economics, safety concerns, and limited bankability. New electrolytes and longer-running installations have begun to mitigate concerns and have proven particularly useful in remote locations—especially island communities and those in which the grid is less reliable—as well as in connection to municipal grids in the United States (e.g., WA, MA), many of which are cofunded by the DOE's Office of Electricity Delivery and Energy Reliability.

Redox flow batteries consist of a few major components: tanks of charged (or to-be-charged) electrolytes, electronics to do the charging (discharging), membranes to separate the electrolyte solutions, and pumps to move liquids around. In commercial vanadium-based species, systems installed by Japan-based Sumitomo Electric Industries are still successfully in operation decades in, but the cost of materials limits overall economic viability. Replacing current vanadium-based electrolytes with those containing organic redox materials is thought by many to be a route to obtaining more commercially competitive flow batteries. While some groups are focused on organics in aqueous solutions of various pHs, others have explored nonaqueous electrolytes. In the latter case, a major advantage stems from the increase in the stability window of aprotic, nonaqueous electrolytes, which may be about 3 times (possibly 4 times) greater than that of aqueous solutions. The result would be—if all other performance metrics are

equal—smaller footprint batteries. Given the massive sizes of these batteries, realizing smaller footprints would greatly assist in their ease in installation in existing communities. To provide an example, the company UniEnergy advertises that “a compact footprint of only five 20' containers” are required to deliver 600 kW of power and 2.2 MWh maximum energy (Figure 1).¹

The bane of many a flow battery chemist's existence is the performance of the membrane that separates the positive and negative solutions, called the posolyte (or catholyte) and negolyte (or anolyte). Separating the components of these solutions from one another is critical to keeping charged components (and their neutral versions) in the appropriate tanks. If species crossover occurs, capacity losses of 50% are inevitable. In acidic aqueous flow batteries, membranes—albeit expensive—exist for keeping species in their respective tanks, but for other pHs and for nonaqueous electrolytes, membranes are still in development. Researchers can choose to wait for better membranes, work on developing better membranes, or—in the case of Hendriks et al.—can tailor the electrolyte for a size exclusion approach. In the latest work from the Sanford group at the University of Michigan, with collaborators Helms, Sigman, and Minter, a dual approach is reported: the combination of an oligomeric posolyte (or catholyte) with a membrane composed of polymers exhibiting intrinsic microporosity (PIMs).²

In their recent publication in *ACS Central Science*, Hendriks et al. report the synthesis and characterization of tris(dialkylamino)cyclopropenium oligomers, some of which are represented in the chemical drawing below.² The oligomers were prepared to evaluate their performance with size exclusion membranes composed of PIMs. By increasing the molecular weight of the oligomers in tandem with decreasing membrane pore size through cross-linking, the authors hoped to minimize membrane crossover of this active species. A recent publication by coauthor Helms showed that the PIMs limited the crossover of other oligomers containing redox-active viologen,

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Figure 1. The 1 MW/4MWh Uni System installed at Schweitzer Engineering Laboratories in Pullman, Washington. Credit: <http://uettechnologies.com>.

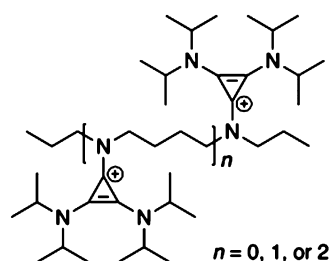


Figure 2. A representation of the chemical structures of select oligomers reported by Hendriks et al.² where the counteranion is hexafluorophosphate.

pyridinium, and alkoxyarene oligomers.^{3,4} The stability of Sanford's tris(dialkylamino)cyclopropenium redox moiety prompted the team to study it as an oligomeric material with a PIM separator (Figure 2).⁵

This systematic study first involved a comparison of oligomers in which spacer distance was varied, allowing the team to systematically evaluate the impact of linker length on the electrochemical potential and stability of these molecules.

This systematic study first involved a comparison of oligomers in which spacer distance was varied, allowing the team to systematically evaluate the impact of linker length on the electrochemical potential and stability of these molecules. The authors found that a minimum linker length of four carbons was needed to isolate redox couples from one another. Next, larger units were explored to measure crossover. While previous results evaluating oligomeric active materials with PIM-based membranes showed that increases in oligomer size and cross-linking content limited crossover to undetectable limits, the stability of the redox species was not extensively probed. Here, Sanford and co-workers construct a full flow cell containing the oligomeric electrolyte for the positive electrode

(posolyte) with a monomeric negolyte (they note that a stable oligomeric negolyte has not been developed). Cycling of these solutions showed rapid capacity loss due to negolyte cross-over—not a surprise given the small size of the active species—but that the posolyte remained stable and on its original side of the membrane.

In summary, the authors present an exciting study in which a modified membrane and oligomerized active material function in a flow battery without crossover, providing a possible solution to a problem that has plagued groups working with nonaqueous electrolytes. I look forward to these authors' future work in the identification of a stable oligomeric negolyte with which to pair their tris(dialkylamino)cyclopropenium materials.

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