

Effect of Current Collector-Cathode Interface on the Charge Transfer Processes in Stable Free-Radical Organic Polymer Cathode Materials

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Organic radical batteries (ORBs) comprise a relatively new technology that uses cathodes based on stable polymeric organic radical-based polymers. These materials show great promise as cathodes in batteries because the neutral, radical species (at left, Figure 1) is remarkably stable and the one-electron oxidation depicted is fully reversible. The rate at which charge can be pushed into or extracted from an electrode is determined by the timescales on which charges are able to move within an electrode and across an electrode-electrolyte, electrode-current collector interface. This work focused on various cathode organic radical-binder composites to determine how the charge/discharge processes based on the radical polymer's redox reaction would be influenced by the interfacial interaction at the aluminum current collector to the organic radical polymer.

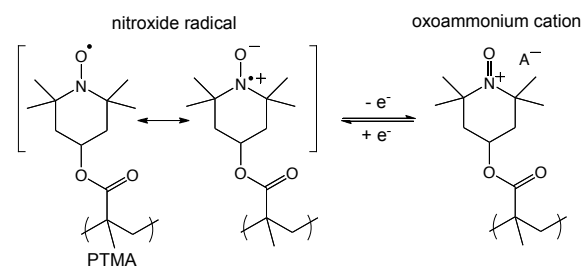


Figure 1: Reversible oxidation/reduction process for a stabilized nitroxide radical PTMA, poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl)

With the Redox process shown in Figure 1, the expansion-contraction of the polymer by the inclusion-exclusion of the solvated anions during charge-discharge can have a direct effect on the adhesion of the cathode matrix to the current collector. Therefore, both the adhesion and the rate of the interfacial charge transfer are important to this study and may be affected by; nitroxide radical concentration i.e. cathode capacity, pendant group chain length, cathode thickness and current collector surface.

AC impedance measurement of the composite electrodes revealed a correlation between: the overall electron transfer resistance of the composite electrode and the material of the current collector; capacity of nitroxide polymer; and the composition of binder. These data suggest that the electric conduction to the current collector through the contact resistance is crucial and can be affected by several different experimental parameters.

We have observed that the adhesion and the contact area

between the composite electrode and the current collector strongly influence the contact resistance. Overall, our results indicate that the charge/discharge performance of the radical battery can be dominated by the interfacial electron transfer processes at the current collector interface. A composite electrode, which has a high adhesion to the current collector, shows a small overall electron transfer resistance and allows for mechanistic investigations of the charge/discharge processes. Therefore, the overall performance of these new organic cathode materials could be improved by suitably designing the interfacial structure for specific charge-discharge rate requirements to maximize interfacial charge transfer through distinct composition for maximal adhesion, minimal polymer expansion and maximized contact sites.

For example, in order to investigate the effects of polymer morphology on ion-charge transport and adhesion at the current collector we investigated a range of nitroxide concentrations in the polymer matrix. Specifically 100 mol% PTMA (TEMPO-100), 60 mol% PTMA – 40 mol% PMMA (TEMPO-60), and 20 mol% PTMA – 80 mol% PMMA (TEMPO-20) were investigated. We found that the decrease in theoretical capacity by reducing the content of the redox active nitroxide radical, altered the charge transfer process via an apparent variation in molecular rearrangement of the polymer pendant groups. We also coated the aluminum current collector with thin films of conductive oxides such as ITO, FTO and IZO as well as graphene layers to enhance adhesion and charge transfer. Finally the effects of solvation spheres and charge density of polymer expansion and adhesion through the use of anions with a range of charge densities, e.g., PF_6^- , ClO_4^- , BF_4^- , and F^- , were also investigated.

The detailed electrochemical investigation including cyclic voltammetry, AC impedance and Spectroelectrochemical Raman studies will be presented.

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