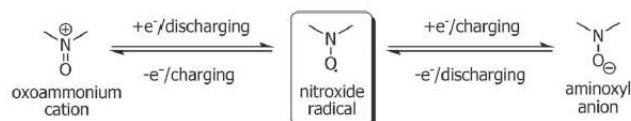


“Ion Transport in Polymeric Nitroxide-Radical Organic Materials”

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Polymeric organic nitroxide radical materials such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) are of great interest for various energy storage applications. These materials are readily synthesized from environmentally benign precursors, and TEMPO in particular has been shown to have very fast charge transfer kinetics.[1, 2] The oxidation of TEMPO in a lithium ion battery is accompanied by an anion from the electrolyte solution diffusing into the polymer network to maintain charge neutrality, and the reduction process can be driven all the way to the formation of the nitroxide anion with the diffusion of a lithium cation ( $\text{Li}^+$ ) into the polymer network. (Figure 1)

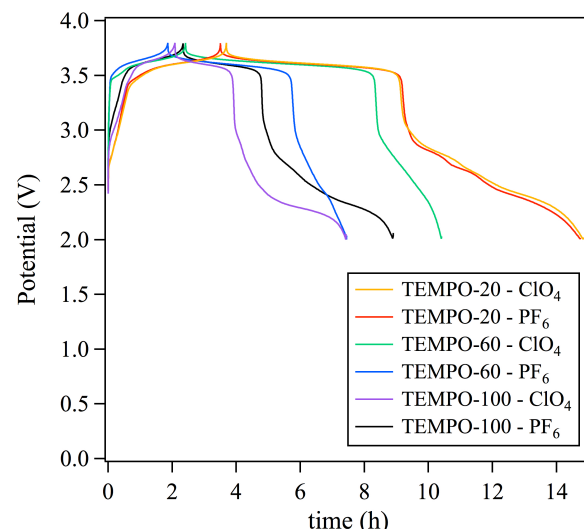


**Figure 1: Reversible oxidation/reduction process for a stabilized nitroxide radical.<sup>1</sup>**

We have used a synergistic experimental-theoretical approach to investigate the interfacial and interstitial charge-transport mechanism of both electrolyte anions and  $\text{Li}^+$  cations for the TEMPO-based polymer poly(2,2,6,6-tetramethylpiperidine methacrylate) (PTMA). Density functional theory calculations of the binding energies of several anions, e.g.  $\text{F}^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ , and  $\text{PF}_6^-$ , with oxidized TEMPO have been carried out and demonstrate a novel correlation to the charge transfer resistances calculated from ac impedance spectroscopy. We have also prepared PTMA polymers over a systematic range of nitroxide radical compositions in order to investigate the effects of polymer morphology on ion charge transport. Results from 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.

In order to focus on the transport processes taking place in the TEMPO electrode, half cells were prepared using lithium foil as the anode. The discharge process was driven from 3.8 V to 2.0 V in order to encompass the oxidation and the reduction of the nitroxide radical. (Figure 1) Data collected from half-cells prepared with TEMPO-20, TEMPO-60, and TEMPO-100 are shown in Figure 2. While all of the cells were cycled at the same rate, the charge and discharge kinetics of the TEMPO-20 cells were significantly reduced. The molecular packing simulations indicate that the configuration adopted by the TEMPO-20 polymer is distinctly different from the TEMPO-60 and TEMPO-100 polymers. The charge and discharge capacities of the TEMPO-20 cells cycled with both  $\text{ClO}_4^-$  and  $\text{PF}_6^-$  were greater than the theoretical

capacity of 35 mAh/g. Conversely the capacities of the TEMPO-60 and TEMPO-100 cells are well below the theoretical capacities of 77 mAh/g and 101 mAh/g respectively.



**Figure 2. TEMPO - lithium half-cells cycled at 0.4 C charge and 0.1 C discharge rates.**

AC impedance data were collected from the cells before and after charging at 0.4C and discharging at 0.1, 0.2, or 0.4C. The cells were cycled repeatedly at each discharge rate until the Nyquist plot was constant. There were no significant changes between the Nyquist plots obtained after the cells had stabilized at the 0.1 C discharge rate. The Nyquist plots for all of the cells intersect the real impedance axis at the same point, indicating that the electrolytes containing different anions produce the same inherent electronic resistance in the cells. Variations in the width of the first semi-circle indicate that the ionic charge transfer resistance varies with both the concentration of the TEMPO unit and the electrolyte anion employed. These results along with the theoretical predictions will be discussed at length.

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