Charge Transport within Radical Redox Polymers as Electroactive Materials in Thin Film Batteries

Hiroyuki Nishide
Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan
Phone: +81-3-3200-2669, Fax: +81-3-3209-5522. Email: nishide@waseda.jp

Radical polymer is an aliphatic or non-conjugated polymer bearing densely populated robust radical substituents as pendant groups per repeating unit. We report that stable radical polymers provide a new class of redox polymers, characterized by a fast kinetics of electrode reactions. Radical groups such as NO-centered nitroxides and O-centered phenoxyls and galvinoxyls were examined as the pendant group of the radical polymer. These radicals were characterized by a rapid and reversible $1e^-$ redox reactions, with heterogeneous electron-transfer rate constants up to 10^{-1} cm/s under suitable conditions. A variety of polymer backbones were employed to bind the radicals, such as polystyrene derivatives and polynorbornenes. Electrochemical behaviors of the polymer membranes attached to the electrode revealed an efficient charge propagation process within the membrane by a site-hopping mechanism. The redox process of the polymer membrane was accompanied by the rapid incorporation of solvated counter ions that compensated the charges produced by the redox reaction (Figure 1).

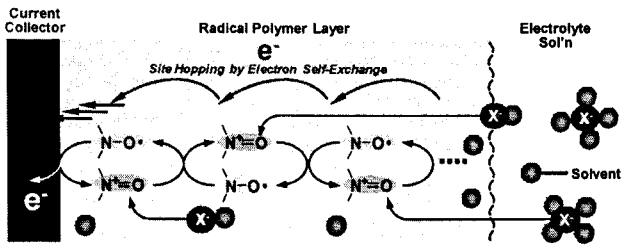

Fig. 1 Electron and mass transfer within the radical polymer membrane.

Fig. 2 A radical polymer battery.

A couple of polymers, different in redox potentials, were used as the electroactive materials to fabricate a thin film battery. The typical combination was the TEMPO-substituted polymer for the cathode, and the phenoxyl-substituted polymers for the anode. The radical polymers were reversibly converted to the corresponding polyelectrolytes. The rapid electrode reaction and the efficient charge propagation led to a high rate performance. The amorphous polymer membrane allowed fabrication of a transparent layer of the electrode-active material (Fig. 2). Challenges toward high-density and burst-power generation by molecular design of the radical polymers will be described.

References

1) H. Nishide, K. Oyaizu, *Science*, **319**, 737 (2008).
2) Y. Yonekuta, K. Susuki, K. Oyaizu, K. Honda, H. Nishide, *J. Am. Chem. Soc.*, **129**, 14128 (2007).
3) T. Suga, H. Konishi, H. Nishide, *Chem. Commun.*, 1730 (2007).