

Organic Radical Battery: Nitroxide Radical Polymers as a Cathode Active Material

Shigeyuki Iwasa,¹ Masahiro Suguro,¹ Nobuhiro Natori,²
Kentaro Nakahara,¹ Jiro Iriyama,¹ Masaharu Satoh,¹
and Hiroyuki Nishide²

¹Fundamental and Environmental Research Laboratories,
NEC Corporation,

34, Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

²Department of Applied Chemistry, Waseda University,
Shinjuku, Tokyo 169-8555, Japan

E-mail: s-iwasa@cd.jp.nec.com

The consumption of electric power in mobile equipment is increasing with the progress of communication systems. There is a great demand for high-energy and/or high-power-density batteries as power sources. Innumerable research efforts have been made toward developing rechargeable batteries with high-energy and high-power density.

Nitroxide radicals are the most persistent and stable species among organic radicals. They have attracted great interest because of their stability and paramagnetic properties applicable to the spin labels, organic ferromagnets, etc. In addition, nitroxide radicals are known to be electrochemically oxidized and reduced (Figure 1). We have proposed “organic radical battery” in which stable organic radicals such as a nitroxide radical are applied to the electrode active material of the rechargeable battery.¹ The excellent rate characteristic and cycle ability of the rechargeable battery using the cathode composed of poly(2,2,6,6-tetramethylpiperidine-*N*-oxy-4-yl methacrylate) (PTMA) have been demonstrated.

In this work, we report syntheses of the nitroxide radical polymers (Figure 2) and their electrochemical properties as an electrode active material. Poly(2,2,6,6-tetramethylpiperidine-*N*-oxy-4-yl acrylate) (PTAA) is an acrylate polymer bearing TEMPO. Poly(2,2,3,3-tetramethylethylenenitroxide) (PTMNO) is the linear aliphatic polynitroxide. Poly(1-(*N*-*t*-butylnitroxy)-3,5-phenylene) (PBNP) is the polyphenylene derivative having nitroxide radical. The theoretical capacity value of these polymers are 119 Ah/kg in PTAA, 224 mAh/kg in PTMNO, 165 Ah/kg in PBNP, and 111 Ah/kg in PTMA. PTAA was synthesized by the anionic polymerization of the acrylate monomer having TEMPO by *s*-BuLi. PTAA was insoluble to electrolyte such as dimethyl carbonate and ethylenecarbonate. PTMNO was synthesized by the cationic ring-opening polymerization of the cyclic amine, following by the oxidation. The formation of nitroxide was confirmed by oxidation of poly(2,2,3,3-tetramethylethylenimine). PBNP with 0.5 spin per the repeating unit was synthesized by the homocoupling reaction and the oxidation of hydroxyl amine. Nitroxide polymer/carbon composite electrodes were prepared from the mixture of nitroxide polymer, graphite powder, and polytetrafluoroethylene powder. The redox potential of PTAA electrode was equal to that of PTMA electrode (0.81 V vs. Ag/AgCl (about 3.6 V vs. Li/Li⁺)). A coin cells (nitroxide polymer/Li metal cell) were fabricated with nitroxide polymer electrode, a separator film, and Li metal as an anode. The PTAA/Li metal cell demonstrated an average discharge voltage of 3.6 V and a discharge capacity of 82 Ah/kg, which corresponds to 70% of the theoretical capacity. The PBNP/Li cell discharged at 3.4 V with a capacity of 71 Ah/kg. An obvious voltage plateau is evident in each discharge curve. In PTAA/Li cell the discharge capacity at 100 C

rate retained 70% of that found for 1C rate measurement.

Acknowledgement

This work was performed as part of the high power density organic radical battery project for data-backup and was supported by the New Energy and Industrial Technology Development Organization (NEDO).

Reference

1. N. Nakahara, et al., *Chem. Phys. Lett.*, **359**, 351 (2002).

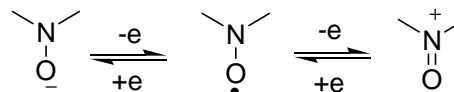


Figure 1. Redox systems of nitroxide.

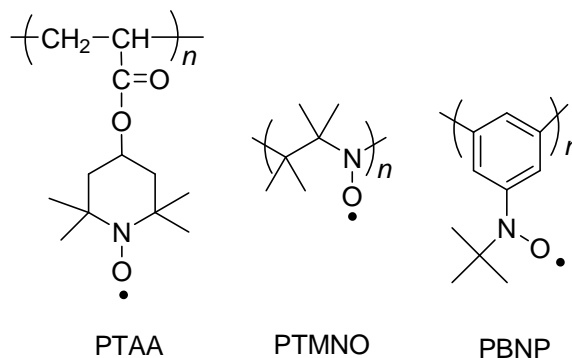


Figure 2. Chemical structures of nitroxide polymers.

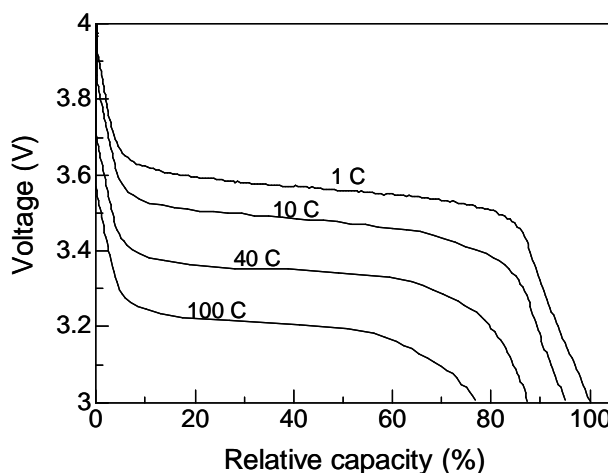


Figure 3. Discharge curves of PTAA/Li coin cell at various rate.