



## Short communication

## Electrochemical properties of new organic radical materials for lithium secondary batteries

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## ABSTRACT

The use of ionic liquid (IL)-supported organic radicals as cathode-active materials in lithium secondary batteries is reported in this article. Two different types of IL-supported organic radicals based on the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical and imidazolium hexafluorophosphate IL were synthesized. The first type is a mono-radical with one unit of TEMPO and the second is a symmetrical di-radical with 2 U of TEMPO; both are viscous liquids at 25 °C. The radicals exhibit electrochemical activity at ~3.5 V versus Li/Li<sup>+</sup> as revealed in the cyclic voltammetry tests. The organic radical batteries (ORBs) with these materials as the cathode, a lithium metal anode and 1 M LiPF<sub>6</sub> in EC/DMC electrolyte exhibited good performance at room temperature during the charge–discharge and cycling tests. The batteries exhibited specific capacities of 59 and 80 mAh g<sup>-1</sup> at 1 C-rate with the mono- and di-radicals as the cathodes, respectively, resulting in 100% utilization of the materials. The performance degradation with increasing C-rate is very minimal for the ORBs, thus demonstrating good rate capability.

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## 1. Introduction

Organic radical batteries (ORBs) that employ stable radicals as electrode-active materials are an area of contemporary interest. In the first report on ORBs, Nakahara et al. demonstrated that poly(2,2,6,6-tetramethylpiperidinyloxy-4-ylmethacrylate) (PTMA), a stable polymer with the nitroxyl radical in the repeating unit, could be employed as a positive electrode material for lithium secondary batteries [1]. Most of the studies reported so far on ORBs have employed PTMA as the cathode-active material [2–10]. Polyacetylene and polynorbornene derivatives carrying the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical have also been synthesized and evaluated as possible electrode materials [11].

The use of such radicals as cathode-active materials is based on the electrochemical oxidation of the nitroxyl radical to the oxoammonium cation. The oxygen-centered nitroxyl radical, TEMPO, has good chemical stability and a highly localized density of unpaired electrons. TEMPO is reported to show redox behavior in aprotic sol-

vents [12]. It is also known to be oxidized electrochemically at 3.5 V versus lithium [1,2]. Since this reaction is reversible in an aprotic electrolyte, it can be used as the cathode reaction in lithium rechargeable batteries. In addition, nitroxyl radicals are known to exhibit a very rapid electron transfer process with a rate constant as high as 10<sup>-1</sup> cm s<sup>-1</sup> [13]. This important characteristic of the material means that it would support fast electrode reactions even at high current densities. Further, the high reactivity and reversibility of the radical reaction make it possible to develop ORB devices with rapid charging ability and high cyclability [14]. ORBs with nitroxyl radical-based electrodes are thus capable of exhibiting remarkable rate capability.

Since solution-based methods are generally adopted for the fabrication of cathodes for use in thin and flexible batteries, it follows that the radical polymer should have good solubility in the common solvents that are used. For the preparation of a PTMA-based cathode by the solution method, *N*-methyl pyrrolidone (NMP) [4,6,8,9] and water [5,7] were used as the solvents in earlier studies. Although the solution casting method has been reported to yield satisfactory results, the uniform dispersion of the solid polymeric radicals in the solvent might not always be achieved, especially if the cathodes are fabricated with a higher active material content. Polymeric radicals such as PTMA do not have good film forming properties either. Thus, Suga et al. recently adopted the photocrosslinking method to pro-

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duce a cathode-active film consisting of a TEMPO-based material with a polynorbornene backbone [15]. However, such procedures are cumbersome and the sensitivity of the nitroxyl radical to most crosslinking agents demand the rather precise control of the whole process, which might not be possible on a large scale.

The use of a liquid organic radical would be highly advantageous to circumvent the difficulties of processing that are presently encountered with polymer radicals. There have been a few studies reported in the literature on the use of TEMPO-derived, task-specific ILs (where the IL-type part maintains the physical properties, while the attached extra function is designed for the specific property) as catalysts for the oxidation of alcohols [16,17]. Since ILs possess the attractive features of a negligible vapor pressure and high thermal stability, they are particularly suitable for electrochemical applications [18]. ILs based on the imidazolium [19–22], pyrrolidinium [23,24] and piperidinium [25,26] cations have been found to be promising electrolyte components for rechargeable batteries. However, no studies have been reported so far on the use of IL-supported organic radicals as the electrode-active material for lithium batteries. In this article, we present encouraging results on the possible use of two types of task-specific ILs as cathode-active materials. These compounds contain the imidazolium cation and hexafluorophosphate anion as the ionic part, which can increase the ion conductivity within the cathode, and the

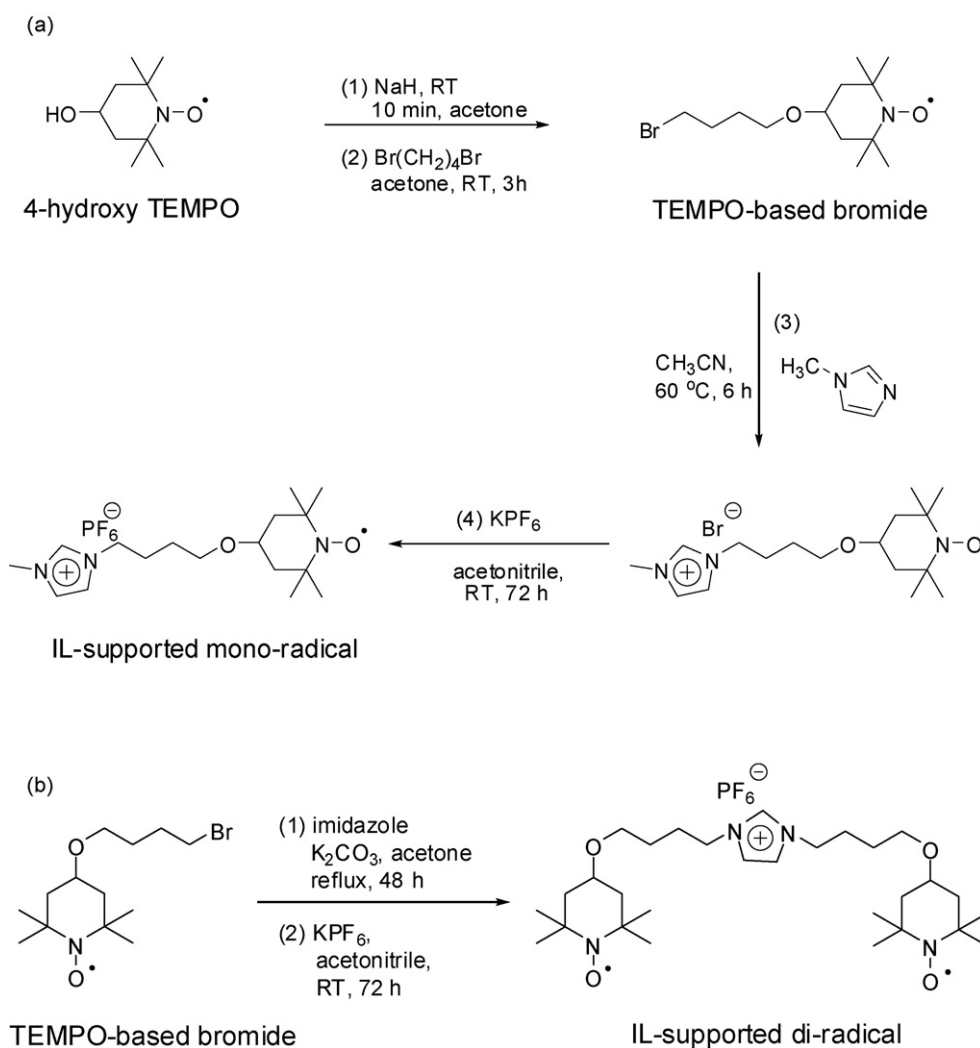
TEMPO-derived radical which imparts the required electrochemical activity.

## 2. Experimental

As shown in Scheme 1, the IL-supported, TEMPO-based radicals used in this study were prepared by a similar method to the one reported by Qian et al. [17]. The IL-supported radicals were characterized by spectral analyses. The  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded on Varian 300 spectrometers using TMS as an internal standard and phenylhydrazine as a radical quencher.

(a) Synthesis of the mono-radical, 1-methyl-3-(4-(2,2,6,6-tetramethyl 1-oxyl-4-piperidoxyl)butyl)imidazolium hexafluorophosphate: the reaction of 4-hydroxy-TEMPO with 1,4-dibromobutane in the presence of NaH at 25 °C for 3 h afforded the TEMPO-based bromide. The quaternization of 1-methylimidazole with the TEMPO-based bromide in acetonitrile at 60 °C for 6 h and subsequent anion exchange with  $\text{KPF}_6$  in  $\text{CH}_3\text{CN}$  for 72 h at 25 °C yielded the wanted IL-supported mono-radical.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.15 (s, 6H), 1.21 (s, 6H), 1.35–1.46 (m, 2H), 1.52–1.60 (m, 2H), 1.87–1.97 (m, 4H), 3.47 (t,  $J=5.7$  Hz, 2H), 3.50–3.61 (m, 1H), 3.87 (s, 3H), 4.17 (t,  $J=7.2$  Hz, 2H), 7.36 (s, 2H),



**Scheme 1.** Synthesis of (a) mono-radical, 1-methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium hexafluorophosphate and (b) di-radical, 1,3-bis(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium hexafluorophosphate.

8.57 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 20.77, 26.53, 27.72, 32.20, 36.45, 44.83, 50.09, 59.87, 67.47, 70.91, 122.43, 123.71, 136.19.

(b) Synthesis of the symmetrical di-radical, 1,3-bis(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium hexafluorophosphate: the reaction of imidazole with two equivalents of the TEMPO-based bromide in the presence of  $\text{K}_2\text{CO}_3$  and subsequent metathesis with  $\text{KPF}_6$  afforded the IL-supported di-radical.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.21 (s, 12H), 1.31 (s, 12H), 1.40–1.62 (m, 8H), 1.78–2.04 (m, 8H), 3.43 (t,  $J$  = 6.3 Hz, 2H), 3.49 (t,  $J$  = 5.7 Hz, 2H), 3.54–3.65 (m, 2H), 4.22 (t,  $J$  = 7.5 Hz, 4H), 7.36 (s, 2H), 8.88 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 20.83, 26.59, 27.77, 32.39, 44.91, 50.09, 59.47, 67.43, 71.01, 122.61, 135.54.

Thermal analyses were performed by differential scanning calorimetry (DSC: TA 2040) in an  $\text{N}_2$  atmosphere in the temperature range of  $-40$  to  $150^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$  and thermogravimetric analysis (TGA: SDT Q600 TA, USA) in  $\text{N}_2$  from  $25$  to  $400^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . Morphological observation was performed by scanning electron microscopy (SEM: JEOL JSM 5600).

The radical-based cathode was fabricated by blending the active material, conductive carbon (Super-P: Aldrich) and poly(vinylidene fluoride) (PVdF: Aldrich) binder at a ratio of 30:60:10 by weight. The components were mixed thoroughly in NMP solvent at room temperature by ball milling for 30 min and the viscous slurry so obtained was cast on aluminum foil and dried at  $60^\circ\text{C}$  under a vacuum for 12 h. The thin film so prepared (thickness of  $\sim 20\ \mu\text{m}$ ) was cut into circular discs with an area of  $0.95\ \text{cm}^2$  and mass of  $\sim 2.5\ \text{mg}$  to evaluate its use as a cathode material. Two-electrode electrochemical coin cells were assembled with a lithium metal ( $300\ \mu\text{m}$  thickness, Cyprus Foote Mineral Co.) anode, radical cathode and Celgard<sup>®</sup> 2200 separator injected with  $30\ \mu\text{L}$  of  $1\ \text{M LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) electrolyte. The cell was assembled under an argon atmosphere in a glove box with a level of  $\text{H}_2\text{O}$   $< 10\ \text{ppm}$ . The charge–discharge and cycling properties of the ORBs were evaluated between 3.0 and 4.0 V at different current densities using an automatic galvanostatic charge–discharge unit, WBCS-3000 battery cyler (WonA Tech. Co.), at  $25^\circ\text{C}$ . Cyclic voltammetry (CV) measurements of the cell were conducted at a scan rate of  $5\ \text{mV s}^{-1}$  between 2.5 and 4.4 V.

### 3. Results and discussion

The chemical structures of the synthesized IL-supported organic radicals were confirmed by spectral analyses (see Section 2). The IL-supported radicals are orange-red colored, viscous liquids at room temperature with an oily appearance. The DSC analyses indicated the existence of endothermic transitions at around  $-10^\circ\text{C}$  for both radicals corresponding to their freezing temperatures. The TGA results showed that they had good thermal stability with a decomposition temperature  $> 240^\circ\text{C}$  (corresponding to 5% decomposition of the sample). Thus, their thermal properties indicate the suitability of these radicals for use over the wide temperature ranges that are generally encountered in battery applications.

The CV curves of the lithium batteries with the mono- and di-radical-based cathodes are shown in Fig. 1. The evaluation of the electrochemical properties of several nitroxyl radical compounds in aprotic electrolytes has shown that they exhibit reversible redox behavior similar to that of TEMPO, independent of their structures, at  $\sim 3.6\ \text{V}$  versus  $\text{Li/Li}^+$  [27]. The two types of IL-supported, TEMPO-based radicals employed in the present study also show a singlet redox couple with an active voltage in the same range. The anodic and cathodic peaks are at 3.6 and 3.5 V, respectively, with a very low redox peak separation of 100 mV. This narrow peak separa-

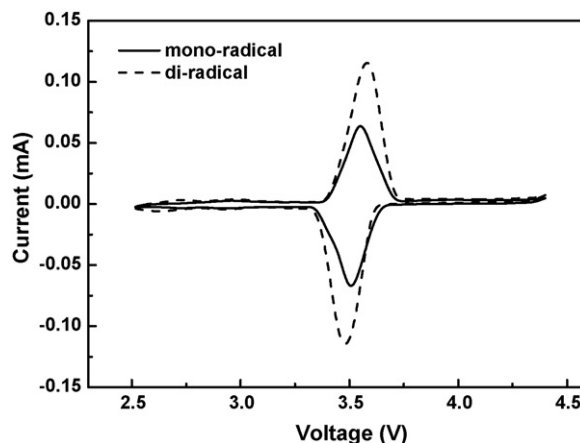


Fig. 1. CV curves of the IL-supported radical-based materials as cathodes in lithium cells ( $25^\circ\text{C}$ ,  $5\ \text{mV s}^{-1}$ , 2.5–4.4 V).

tion results from the capability of nitroxyl radicals for fast reaction kinetics. The symmetric oxidation and reduction peaks with comparable areas indicate that they have a high coulombic efficiency for the charge–discharge process. The CV curve for the di-radical shows a larger redox peak with a higher current compared to that of the mono-radical, due to the higher capacity of the former. The theoretical capacity of the mono-radical is calculated to be  $59\ \text{mAh g}^{-1}$  based on its molecular weight of 454, with a single electron available for the redox reaction, whereas the di-radical with a molecular weight of 666 and 2 electrons participating in the redox process has a higher theoretical capacity of  $80\ \text{mAh g}^{-1}$ . The CV behaviors of these IL-supported radicals are comparable to that of PTMA, the TEMPO-based acrylate polymer that has been widely studied for developing ORBs [1,7–9].

The electrochemical evaluation of the ORBs with the radicals as cathode-active materials was performed at current densities corresponding to 1, 10 and 20 C-rates at  $25^\circ\text{C}$ . Fig. 2 shows the charge and discharge behavior of the ORB with the mono-radical as the cathode during the first cycle at these C-rates. The charging and discharging processes occur at  $\sim 3.6$  and  $\sim 3.5\ \text{V}$ , respectively, which is in agreement with the observations made earlier based on CV studies. At the lower, 1 C-rate, both the charge and discharge capacities are equal to  $59\ \text{mAh g}^{-1}$ , which correspond to 100% utilization of the active material. At the higher current densities corresponding to the 10 C and 20 C rates, the capacities are 57 and  $56\ \text{mAh g}^{-1}$ ,

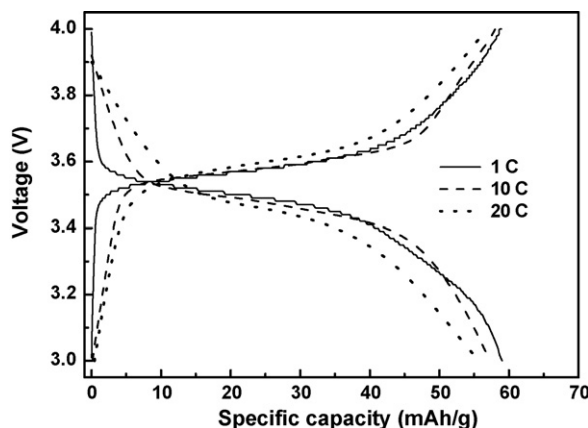


Fig. 2. Initial charge–discharge curves of lithium batteries with mono-radical-based cathode at different C-rates ( $25^\circ\text{C}$ , 3.0–4.0 V).

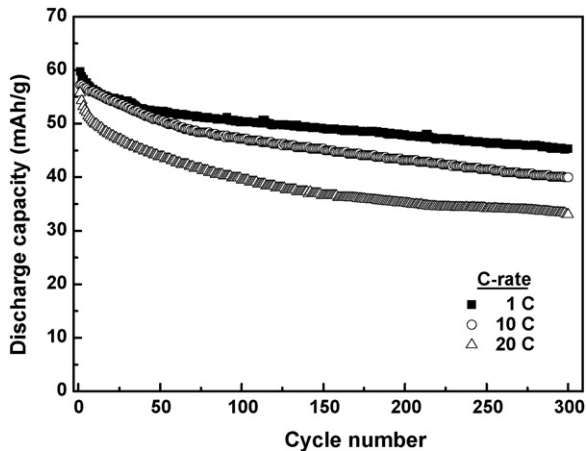


Fig. 3. Cycle performance of lithium batteries with mono-radical-based cathode at different C-rates (25 °C, 3.0–4.0 V).

respectively, which are >94% of that at 1 C. The high-power rate capability of the ORB with the mono-radical is thus evident from this data. The earlier studies on ORBs with PTMA-based cathodes reported their remarkable power-rate capability and attributed it to the fast electron transfer kinetics of the nitroxyl radical [1–3,8], which is also applicable in the case of the IL-supported radicals used in this study. The charge capacities agree well with the respective discharge capacities at all three C-rates, indicating the high coulombic efficiency of the redox process in the battery.

The cycle performances of the ORB with the mono-radical-based cathode at different C-rates are compared in Fig. 3. During the initial cycles, a decrease in the discharge capacity is observed, probably due to the initial interactions of the electrolyte at the lithium electrode, which would form an interface restricting the free movement of the ions. As the cycling advances, the performance of the ORB also stabilizes, indicating the formation of stable electrode/electrolyte interfaces in the cell. Thus, after 300 charge–discharge cycles at 1, 10 and 20 C rates, the ORB exhibits discharge capacities of 45, 40 and 33 mAh g<sup>-1</sup>, respectively. These values correspond to retentions of 76, 70 and 59% of the initial capacities, respectively, at the above C-rates.

The as-prepared mono-radical-based cathode exhibits a uniform morphology, as shown in Fig. 4(a). The spherical particles of carbon with a size of ~40 nm are covered with a thin layer of the mono-radical and binder. Being a viscous liquid, the active material is uniformly distributed within the cathode matrix. No appreciable change in the morphology was observed even after

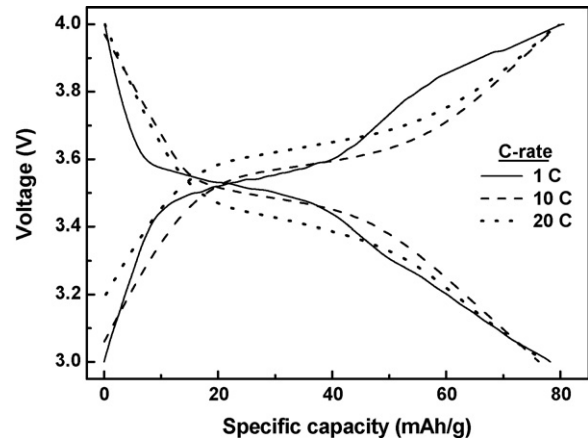


Fig. 5. Initial charge–discharge curves of lithium batteries with di-radical-based cathode at different C-rates (25 °C, 3.0–4.0 V).

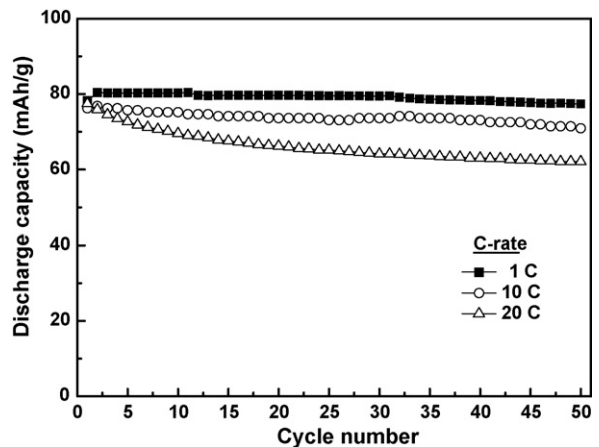


Fig. 6. Cycle performance of lithium batteries with di-radical-based cathode at different C-rates (25 °C, 3.0–4.0 V).

100 charge–discharge cycles at 1 C-rate, as shown in Fig. 4(b). The SEM observation thus provides evidence for the homogeneity of the cathode structure and its retention during the cycling of the cell, which supports the power-rate capability of the ORB.

The results of the electrochemical evaluation in terms of the first cycle charge–discharge properties and cycle performance of the ORB based on the di-radical cathode are presented in Figs. 5 and 6, respectively. The ORB delivers an initial charge

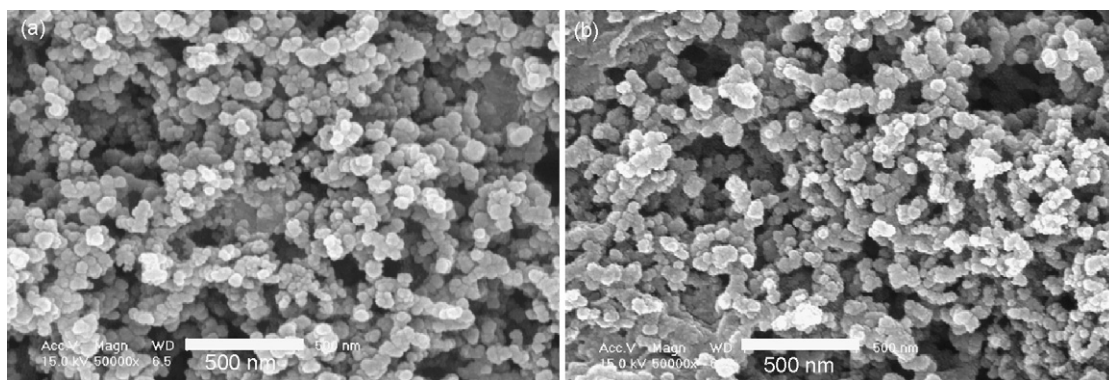


Fig. 4. SEM of mono-radical-based cathode: (a) as-prepared and (b) after undergoing 100 charge–discharge cycles at 1 C-rate (25 °C, 3.0–4.0 V).



capacity of  $80 \text{ mAh g}^{-1}$  and discharge capacity in the range  $80\text{--}77 \text{ mAh g}^{-1}$  at all of the C-rates tested herein, with  $>96\%$  utilization of the active material. The cycling properties at these C-rates were evaluated up to 50 cycles. Excellent cycling performance is observed at 1 and 10 C-rates, with retentions of 99 and 92% of the initial capacity, respectively, after 50 cycles. 80% retention of the initial capacity is achieved after 50 cycles even at the higher, 20 C-rate. The di-radical shows slightly better performance than the mono-radical, particularly with respect to the cycling properties.

Another noteworthy observation concerns the separation ( $\Delta V$ ) between the charge and discharge voltages of the ORBs. It is observed that  $\Delta V$  does not vary substantially with the C-rate for the ORBs based on the radicals studied herein (Figs. 2 and 5). Thus,  $\Delta V$  increases from 0.1 V at 1 C to 0.16 V at 20 C in the case of the mono-radical and from 0.05 V at 1 C to 0.17 V at 20 C in the case of the di-radical. This is an indication of the low ohmic resistance (polarization) of the electrode, which evidently results from the homogeneous cathode structure with sufficient conductivity, making efficient charge transfer possible even under fast reaction conditions. The liquid nature of the radicals used as the active materials contributes to the uniform composition of the cathode, which supports its high-rate capability.

This study reveals that IL-supported radicals can also function as the cathode-active materials of lithium secondary batteries with high-rate capability. When compared to PTMA with its theoretical capacity of  $111 \text{ mAh g}^{-1}$ , the obvious drawback of these IL-supported radicals is their lower capacities. The TEMPO-derived di-radical is more attractive in this respect, since it has a theoretical capacity  $\sim 1.5$  times that of the mono-radical. The chemical structures of such IL-supported radicals may be suitably designed to realize smaller molecules with lower molecular weight and/or higher radical moieties per molecule for the purpose of achieving active materials with higher theoretical capacities. These approaches might lead to the development of IL-supported radicals that are suitable for developing high-energy, high-power ORBs.

#### 4. Conclusions

The evaluation of the electrochemical properties of IL-supported, TEMPO-derived organic radicals as cathode-active materials for lithium secondary batteries is reported herein for the first time. These radicals, which are viscous liquids at room temperature, contain the imidazolium cation and hexafluorophosphate anion. Two types of radical, viz. the mono- and di-radical with theoretical capacities of 59 and  $80 \text{ mAh g}^{-1}$ , respectively, are capable of functioning as very efficient cathode materials for the room temperature operation of ORBs, exhibiting high-rate capability and stable cycling properties. The specific capacities obtained at 1 C-rate correspond to the theoretical capacities and no substantial decrease in capacity is observed at the higher 10 C-rate. These

novel, IL-supported radicals exhibit electrochemical characteristics similar to those of PTMA with the advantage of easier processing.

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