



Short communication

In situ electrochemical-electron spin resonance investigations of multi-electron redox reaction for organic radical cathodes

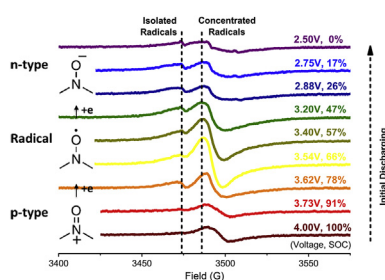
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HIGHLIGHTS

- *In situ* electrochemical-ESR to explore organic radical battery is developed.
- Two-electron redox reaction of PTMA based composite cathode is proved.
- An adjustable n-type doping process of PTMA is observed upon discharging.
- Both concentrated and isolated radicals are found in organic radical cathodes.

GRAPHICAL ABSTRACT



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ABSTRACT

The multi-electron redox reaction of an organic radical based composite cathode comprised of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA)-Ketjenblack is investigated using an *in situ* electrochemical-electron spin resonance (ESR) methodology. The experiments allow each electrochemical state to be associated with the chemical state (or environment) of the radical species upon the cell cycling. *In situ* ESR spectra of the composite cathode demonstrate a two-electron redox reaction of PTMA that is from an aminoxy anion (n-type, at 2.5–2.6 V vs. Li/Li⁺) via a radical (at 3.2–3.5 V vs. Li/Li⁺) to an oxoammonium cation (p-type, at 3.7–4.0 V vs. Li/Li⁺). In particular, an adjustable n-type doping process of PTMA is first observed during the discharging process. Moreover, two different local environments of radical species are found in the PTMA-Ketjenblack composite electrode that includes both concentrated and isolated radicals. These two types of radical species, showing similarities during the redox reaction process while behaving quite different in the non-faradic reaction of ion sorption/desorption on the electrode surface, govern the electrochemical behavior of PTMA based composite electrode.

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1. Introduction

The increasing necessity to develop high performance electrochemical energy storage is driven by the rapid development of

portable electronic devices and electrification of transportation. State-of-art lithium-ion batteries, which have received a lot of attention [1–4], mostly use inorganic energy storage materials with the intercalation concept [5]. This charge transfer mechanism limits the capacity (140–170 mAh g⁻¹), power density, safety and cycle life of batteries. Organic polymer based energy storage materials are an attractive alternative due to their inherent advantages that include: tunable redox property and high theoretical capacity, potentially high energy and power properties by varied charge

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transfer mechanisms, along with the added benefits from polymer materials such as environmentally-benign, light weight, and mechanic (elastic) properties [6,7]. In particular, radical polymers show promise as cathode candidates for lithium-ion batteries [8]. Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) containing a robust nitroxide radical group was first reported as organic radical cathode in 2002 [9,10]. The nitroxide radical, with a resonance structure bearing a localized unpaired electron on the nitrogen and oxygen atoms, provides high chemical stability and two redox couples [10–12]: on the anodic side, the nitroxide is oxidized to form the oxoammonium cation that corresponds to a p-type doping; and on the cathodic side, the nitroxide is reduced to the aminoxyl anion that corresponds to an n-type doping [11,12]. In the reported organic radical batteries, however, the nitroxide polymer based cathode has mostly shown one redox couple on the anodic side (p-type doping) at 3.6 V vs. Li/Li⁺, which results in a low specific capacity of ~100 mAh g⁻¹ [9]. Recently an organic radical composite cathode comprised of PTMA-Ketjenblack (KB), with a two-electron redox reaction, has been developed in our group [13,14]. It was found that the performance of an organic radical electrode is strongly dependent on the conductive carbon material that plays a significant role in the electron transfer through the radical electrode during the charge–discharge process [14–18]. However, there is still a lack of mechanistic investigation on the electrochemical behavior of organic radical cathodes.

Owing to the radical polymers featuring unpaired electrons as the energy storage species in organic radical batteries, electron spin resonance (ESR) spectroscopy has been proposed to explore the charge transfer mechanism of radical polymer based active materials. A pseudo *in situ* electrolytic ESR measurement has been developed to probe the organic radical which was dissolved into the liquid electrolyte while a fixed potential was applied to the electrolytic cell [10,19]. However, an *in situ* ESR tool has not been reported to study organic radical batteries in which the ESR spectrum for a solid state electrode is detected during the cell cycling. In this work, we develop *in situ* electrochemical-ESR and show how this methodology can provide insight into the multi-electron redox reaction mechanism of PTMA-KB based composite cathode by tracking the ESR signal and the electrochemical signal of radical polymer electrode *simultaneously* as a function of time during charge–discharge process.

2. Experimental

2.1. Preparation of PTMA-KB composite electrode

The radical polymer PTMA, employed as the electrode-active material, was prepared according to a published approach [9] with some modifications on synthesis and purification procedures. The PTMA-KB composite electrode was prepared by a simple solvent-less electrode fabrication method [13,14]: PTMA and KB (EC-600JD, AkzoNobel Corp.) were mixed in a planetary mill followed by further milling with PTFE binder. The milled PTMA-KB-PTFE composite powder was rolled into a paper electrode, with a final weight ratio of 16.7:66.7:16.7.

2.2. Preparation and measurements of *in situ* electrochemical-ESR cell

The measurements were performed in an *in situ* cell (Fig. 1a) constructed in a sealed rectangular glass tube (0.8 mm × 8 mm × 100 mm). It contains a working electrode (PTMA-KB composite electrode with a surface area of 1.0 cm² and thickness of 40 μm) and an auxiliary and reference electrode (Li metal) that was positioned as fully as possible outside of the active

region of the ESR resonator (to minimize a background signal from conduction electrons on Li) while keeping a short distance from the working electrode (to minimize the internal impedance of the cell). The flat cell design can facilitate a maximum ESR response with minimum microwave electric field absorption when the cell is placed in the microwave cavity of an ESR spectrometer [20]. The cell was galvanostatically cycled at a current density of 4.5 μA cm⁻² (1/25C rate) with the cutoff potentials of 4.0 and 2.5 V vs. Li/Li⁺ for charge and discharge processes respectively. Meanwhile, the *in situ* ESR measurement was performed by a Bruker Elexsys 580 spectrometer fitted with a SHQE resonator. See the [Supplementary data](#) for the details in ESR measurement.

3. Results and discussion

3.1. Multi-electron redox reaction of nitroxide polymer

The charge–discharge profiles of our developed *in situ* cell (Fig. 1b) display multiple voltage plateaus at 3.5–3.7 V and 2.9–3.2 V respectively, consistent with the multiple redox couples of the cyclic voltammogram in a coin cell [13,14], demonstrating the multi-electron redox reaction of PTMA based composite electrode. The initial discharge capacity of the *in situ* cell is more than 190 mAh g⁻¹ that is the most capacity delivered in a coin cell [13,14]. Moreover, the reversible charge–discharge curves and good capacity retention in the following cycles indicate that the *in situ* cell is able to output the robust electrochemical performance of an organic radical cathode that is comparable to a practical coin cell system.

The ESR spectra of PTMA-Ketjenblack composite electrode were recorded during the charging and discharging of the *in situ* cell (Fig. 1c). Moreover, the double integration of ESR spectrum, which responds to the total radical concentration, was plotted as a function of capacity (Fig. 2). By combination with the charge–discharge profiles, the relationship between the total radical concentration and the voltage of composite electrode is established in the cell cycling process. As shown in Fig. 2a, the experiment started from an open circuit voltage of 3.1 V vs. Li/Li⁺ for the fresh *in situ* cell (labelled as A), with the radical concentration about 80% of its maximum. During the initial charging, the radical concentration increased until 3.6 V where it reached the maximum (B). Then the radical concentration dropped down sharply during the first charge plateau and reached the minimum (C) at 3.8 V, followed by slight increase again when continuously charging to a top cutoff voltage of 4.0 V (D). Here the ESR signal is significantly diminished in the first charge plateau indicating the electron pairing process, i.e. radical species are oxidized to the cations (p-type doping). In the discharging process (Fig. 2b), the radical concentration began with the slight decline until 3.7 V where it reached the minimum (E), and then rose dramatically during the first discharge plateau to reach the maximum (F) at 3.5 V. The regeneration of the radicals suggests that the cations are reduced back to the radical species. With the further discharging, the radical content went through a significant decline starting from 3.2 V (G) and reached the sub-minimum at 2.9 V (H–I) followed by the minimum at the bottom cutoff voltage of 2.5 V (J). The elimination of the unpaired electron once again indicates that the radical species are further reduced to the anions (n-type doping).

The charge–discharge process for the subsequent cycles, as shown in Fig. S1, maintains the two main voltage plateaus at 2.9–3.2 V and 3.5–3.7 V vs. Li/Li⁺ respectively; meanwhile, the double integration of ESR spectrum shows the maximum at 3.2–3.5 V between two main voltage plateaus, and the minimum at 2.5–2.6 V and 3.7–4.0 V respectively in each end of voltage ranges. The *in situ* results demonstrate a two-electron redox reaction of

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