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Short communication

Tris(pentafluorophenyl) borane-containing electrolytes for electrochemical reversibility of lithium peroxide-based electrodes in lithium–oxygen batteries

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HIGHLIGHTS

- ► TPFPB reduces the charge potential of Li_2O_2-based electrode.
- ► TPFPB mitigates the formation of Li_2CO_3 by the electrochemical decomposition of EC and EMC.
- ► The electrochemical reversibility of Li_2O_2-based electrode is improved in the presence of TPFPB.

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ABSTRACT

Tris(pentafluorophenyl) borane (TPFPB) is evaluated as an additive for improving electrochemical performance of lithium peroxide (Li_2O_2)-based electrodes. It is found that TPFPB significantly reduced the charge potential of Li_2O_2-based electrodes during the first charge process and improved reversible capacity during cycling without adding air (or O_2) to the cell. To confirm the effect of TPFPB on electrolyte decomposition, the surface chemistry of Li_2O_2-based electrodes cycled in electrolytes with and without TPFPB was investigated.

1. Introduction

Rechargeable Li–air batteries have attracted much attention as promising candidates for use in electric vehicles because such batteries can theoretically store 5–10 times more energy than current Li–ion batteries [1–3]. However, a significant technical challenge for the implementation of Li–air batteries is to ensure a reversible reaction [2,4]. Li–air batteries rely on the use of oxygen (or, ideally, ambient air) to form the solid products (Li_2O or Li_2O_2) during discharge and oxidation of lithium oxides to lithium and gaseous oxygen, which occurs upon subsequent charging. The insoluble solid reaction products in the organic electrolytes are accumulated within the pores of the air electrode and impede the rechargeability of Li–air batteries [2,3]. To avoid the precipitation of reaction products and the passivation of the electrode surface, appropriate polar solvents are required to dissolve these solid products [5]. Organic carbonate-based electrolytes have been the most widely used electrolyte in Li–O_2 cells [1,2,6]. Such electrolytes, however, decompose in Li–O_2 cells on discharge, rather than forming Li_2O_2, and in the process Li_2CO_3 and lithium-containing compounds are formed in the air electrode [7–9]. Recently, it was reported that organic carbonate-based electrolytes decompose at the cathode and that a mixture of lithium propyl dicarbonate, Li_2CO_3, HCO_2Li, CH_3CO_2Li, CO_2, and H_2O is formed on discharge [7]. In this regard, it was also reported that cyclic and linear carbonates, commonly used solvents in Li–ion batteries, are unstable in the presence of superoxide anion radical ($O_2^{\bullet -}$) [9]. The development of appropriate electrolytes is one prerequisite that is necessary to assure the long term stability of Li–air batteries.

Even though various cathode catalysts including carbon, metal oxides, and noble metals have been applied to enhance the sluggish kinetics of the oxygen reduction reaction and oxygen evolution reaction at the air electrode, Li–O_2 cells still suffer from electrolyte decomposition and insoluble Li_2O_2 clogging the pores of the air

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cathode [4,10–12]. Selecting the optimum nonaqueous solvent for rechargeable Li–air batteries is an essential prerequisite for the successful operation of Li–air batteries. Besides solvents, functional additives can be utilized to dissolve Li_2O or Li_2O_2 solid products. Lewis acid such as tris(pentafluorophenyl)borane (TPFPB) and family of boron esters are expected to dissolve LiF, Li_2O, and Li_2O_2, which are normally insoluble in carbonate-based solvents [12–14]. Importantly, it was reported that TPFPB can partially dissolve insoluble lithium–oxygen products formed at the air cathode and thereby a more active carbon surface can be exposed for further oxygen reduction reaction (ORR) during discharge process [15,16].

Here, we report on the results of an experiment considering the influence of TPFPB-containing electrolytes on electrochemical reversibility of an electrode with Li_2O_2 as the dominant discharge product of Li–air batteries. Additionally, we analyze the effect of TPFPB on the products of Li_2O_2-based electrodes on electrochemical reduction and oxidation.

2. Experimental

For the electrochemical tests, a composite Li_2O_2 electrode was prepared by spreading a slurry mixture of Li_2O_2 (technical grade 90 wt.%, Aldrich), poly(vinylidene fluoride) (PVDF) (KF1100, Kureha Chemical Industry), and super P (as a carbon additive for conductivity enhancement, Timcal Inc.) (35:20:45 in weight ratio) on a piece of Al foil (20 μm). The resulting electrodes were dried at 100 °C for 30 min. The Li_2O_2 loading was 0.13 mg cm^{-2}. The electrolyte was comprised 1.0 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (30:70, v/v) with 5 wt.% tris(pentafluorophenyl) borane (TPFPB) (95 wt.%, Aldrich) and 3 wt.% vinylene carbonate (VC, Soulbrain Co. Ltd.). VC was used as an additive to form an effective solid electrolyte interphase (SEI) layer on the Li electrode.

Galvanostatic discharge and charge cycling (WonATech WBCS 3000 battery measurement system) was performed in the potential window from 2.0 to 4.5 V vs. Li/Li^+ using a two-electrode 2032 coin-type cell without holes for air (or O_2) permeation. Microporous polyethylene film was used as a separator. Cells were assembled in an Ar-filled glove box with less than 1 ppm of both oxygen and moisture. The Li_2O_2 electrode functioned as the working electrode and the Li metal foil as the counter electrode. In order to obtain a proper porosity, the Li_2O_2 electrode was not pressed and was spot-welded to the top of the coin cell.

After cycling, cells were carefully opened in a glove box to retrieve their electrodes, and electrodes were subsequently rinsed in dimethyl carbonate (DMC) to remove residual $LiPF_6$-based electrolyte; resulting materials were dried at room temperature.

To investigate the effect of TPFPB on the dissociation of Li_2O_2 in EC/EMC solvent, ^{11}B nuclear magnetic resonance (NMR) experiments for EC/EMC/0.06 M TPFPB with and without Li_2O_2 were performed on a Bruker 500 MHz FT-NMR spectrometer. For the measurement of ex situ Raman, Attenuated Total Reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), these dried electrodes were utilized. An air-tight Raman cell, which we have developed, was assembled in a glove box filled with high purity argon gas [17]. The Raman spectra were recorded at room temperature using an NRS-5100 micro Raman spectrophotometer (Jasco International Co., Ltd.), which was equipped with a single monochromator as a laser filter. Raman spectra were excited by a 532 nm laser.

Cell impedances of 2032 coin-type cells (Li_2O_2 electrode/metallic lithium) before and after charge were monitored by means of an AC complex impedance analysis with an IVIUM frequency response analyzer over a frequency range of 50 mHz to 1 MHz.

3. Results and discussion

Fig. 1 shows a comparison of the voltage profiles of the Li_2O_2/super P/PVDF and the super P/PVDF electrodes using different electrolytes at 23.4 mA g^{-1} during the first cycle. The large overpotential for the Li_2O_2/super P/PVDF electrode with EC/EMC (3/7, v/v)/1 M $LiPF_6$ is clearly shown in Fig. 1(b) and a low charge capacity of 563 mAh g^{-1} was obtained even after charging to 4.5 V vs. Li/Li^+. Interestingly, the addition of 5 wt.% tris(pentafluorophenyl) borane (TPFPB) to EC/EMC (3/7, v/v)/1 M $LiPF_6$ significantly reduced the charge potential of the Li_2O_2 electrode and led to an increased charge capacity of 1294 mAh g^{-1}, as shown in Fig. 1(a). The reduced charge potential during the first charge may be related to the improvement of the electrochemical oxidation of Li_2O_2 to Li and gaseous oxygen, which is a result of the presence of TPFPB in the electrolyte. It is supposed that the electron deficient boron center in the TPFPB interacts strongly with the O_2^{2-} in Li_2O_2 and thereby, the electrochemical oxidation of Li_2O_2 readily takes place in carbonate-based electrolytes. In order to investigate the dissociation ability of TPFPB for Li_2O_2, the ^{11}B NMR spectra of EC/EMC/0.06 M TPFPB and EC/EMC/0.06 M Li_2O_2 with 0.06 M TPFPB were taken at room temperature, as shown in Fig. 2(a) and (b). The addition of 0.06 M TPFPB in EC/EMC with 0.06 M Li_2O_2 results in a pronounced new peak at an up field shift (−3.82 ppm), as shown in Fig. 2(b). This peak is considered to generate from the ion–dipole interaction between boron of TPFPB and O_2^{2-} of Li_2O_2, reflecting more

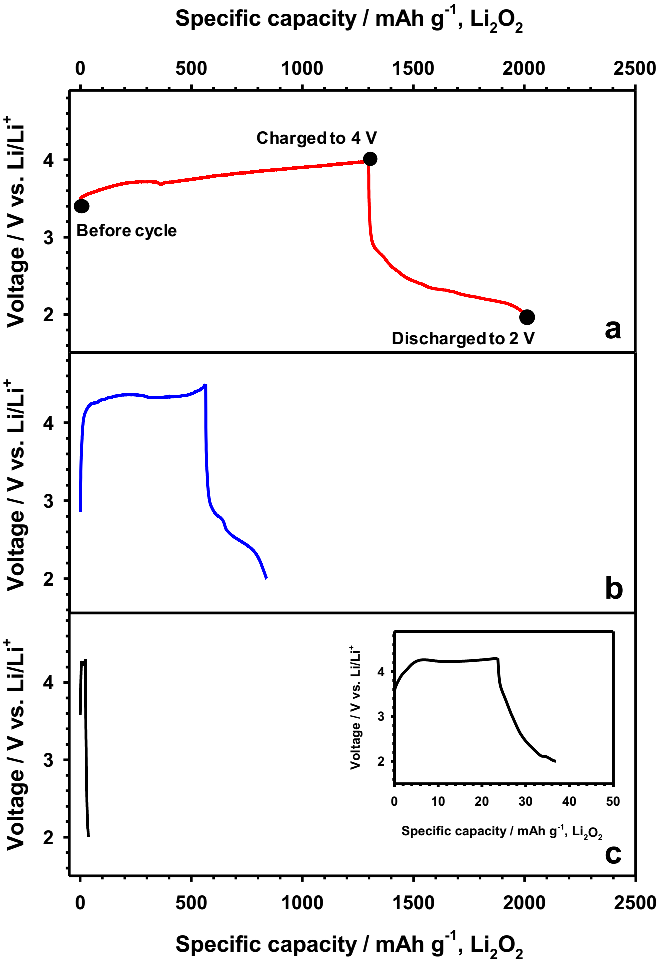

Fig. 1. The voltage profiles of (a) Li_2O_2/Super P/PVDF electrode in EC/EMC/1 M $LiPF_6$ with 5 wt.% TPFPB, (b) Li_2O_2/Super P/PVDF electrode in EC/EMC/1 M $LiPF_6$, (c) Super P/PVDF electrode in EC/EMC/1 M $LiPF_6$ during the first cycle.