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# Tris(pentafluorophenyl) borane as an electrolyte additive for Li-O<sub>2</sub> batteries



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## ABSTRACT

TPFPB was used as an additive in a rechargeable Li-O<sub>2</sub> cell utilizing an electrolyte composed of a solution 1 M LiPF<sub>6</sub> in tetraethylene glycol dimethyl ether (TEGDME) to investigate the effects on capacity and cycling performances. Capacity limitation was also applied to the cells and results were compared with full charging and discharging condition. Galvanostatic charge/discharge (GC) measurements were performed in the assembled Li-O<sub>2</sub> cells using assembled cells, designed with different electrolytes. Cell discharge capacities were cyclically tested by a battery tester at a constant current in voltage range between 2.15 V–4.25 V. Discharge products of the electrolytes characterized by SEM and XRD techniques. The electrochemical results showed increasing discharge capacity and cycleability of the assembled cells produced with TPFPB as compared to TPFPB free electrolytes.

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## Introduction

Due to their high energy densities, Li-O<sub>2</sub> batteries assessed as extremely attractive technology for electrical energy storage. Li-O<sub>2</sub> battery system has high theoretical specific energy of 11 kWh kg<sup>-1</sup> excluding O<sub>2</sub> or about 5.2 kWh kg<sup>-1</sup> when the oxygen weight is included, which provides higher energy density than conventional batteries, almost 10 times that of the state-of-the-art Li-ion battery technology [1]. Li-O<sub>2</sub> batteries are promising candidates for electric vehicles because of their high theoretical specific energies can compete with gasoline [2,3].

Fundamentally, in a Li-O<sub>2</sub> battery system, the electrochemical oxidation of Li metal is expected on the anode during discharge and the reduction by oxygen is expected on the

cathode during charge. Li<sup>+</sup> migration from the anode through an electrolyte and reaction with oxygen at the cathode to form Li<sub>2</sub>O or Li<sub>2</sub>O<sub>2</sub> is a desired occurrence. However, the discharge products such as Li<sub>2</sub>O or Li<sub>2</sub>CO<sub>3</sub> are undesirable because of the irreversible characteristics of those products resulting in clogging of the active cathode pores and prevent access of oxygen [4,5]. To overcome this problem, many researchers have studied materials such as catalysts and binders, structure of electrode materials, and the effect of moisture on the electrodes and reactions [6–9].

The electrolyte has a key role in non-aqueous Li-O<sub>2</sub> batteries in terms of producing the appropriate reversible electrochemical reduction. A suitable electrolyte should have high oxygen solubility, good conductivity, and high stability against superoxide, large potential windows and ability to facilitate the reversibility of discharge–charge cycle by

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solubilizing the discharge products [10]. Tetraethylene glycol dimethyl ether (TEGDME) has favorable properties, such as the high boiling point and low volatility [11] and it is considered to be comparably stable and mainly promoting the formation of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  [12].

Up to now, various cathode catalysts such as carbon, metal oxides, and noble metals have been carried out to improve the poor kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the cathode [7,13]. However,  $\text{Li-O}_2$  batteries still suffer from electrolyte decomposition and insoluble  $\text{Li}_2\text{O}_2$  clogging the pores of the air cathode [8,14–17]. Selecting the optimum non-aqueous solvent for rechargeable  $\text{Li-O}_2$  batteries is an essential prerequisite for the successful operation of  $\text{Li-O}_2$  batteries. Besides solvents, functional additives can be utilized to dissolve  $\text{Li}_2\text{O}$  or  $\text{Li}_2\text{O}_2$  solid products. Several researchers studied tris(pentafluorophenyl) borane (TPFPB) as an electrolyte additive for lithium battery systems and they suggested that improved battery performance was observed by using TPFPB [18–20]. Lewis acid such as TPFPB and family of boron esters are expected to dissolve  $\text{LiF}$ ,  $\text{Li}_2\text{O}$ , and  $\text{Li}_2\text{O}_2$ , which are normally insoluble in carbonate-based solvents [19,21]. 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 [22]. The TPFPB anion receptor binds to peroxide anion and forms a thermodynamically stable species that could be electrochemically oxidized with improved kinetics than the oxidation of solid  $\text{Li}_2\text{O}_2$  on a microporous carbon cathode. The superoxide radical also forms the TPFPB-peroxide anion complex through disproportionation mechanism. Possible reaction of TPFPB with  $\text{Li}_2\text{O}_2$  was given in Fig. 1 [23].

In this study, the effects of tris(pentafluorophenyl) borane (TPFPB) addition to the electrolyte at the gas diffusion layer (GDL) cathode were investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), cycle-ability, SEM and X-ray diffraction (XRD). The introduction of TPFPB into the electrolyte consisting of 1 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in tetraethylene glycol dimethyl ether enhances the capacity retention and coulombic efficiency.

## Experimental details

### Cell assembly

The gas diffusion layers (GDLs) (SIGRACET 24BC, SGL Carbon Inc.) with an area of  $2.54 \text{ cm}^2$  were dried overnight at  $80^\circ\text{C}$ . Anhydrous TEGDME (Alfa Aesar) treated with molecular sieves to remove the impurities prior to use as the electrolyte. Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) (>98.0%) was dried at

$80^\circ\text{C}$  for 72 h under argon atmosphere. A lithium foil disk was used as an anode material and the gas diffusion layer (GDL) was used as a cathode material while glass fiber ( $18 \times 0.65 \text{ mm}$ , ECC1-01-0012-A/L) saturated in the electrolyte was used as a separator. A solution of 1 M  $\text{LiPF}_6$  (Aldrich) in tetra(ethylene glycol) dimethyl ether (tetraglyme, Aldrich) was used as the electrolyte. 1 M  $\text{LiPF}_6$  in TEGDME electrolyte was prepared and 0.1 M TPFPB added to solvent and mixed vigorously by magnetic stirring and stored in amber glass sample vials in an MBraun dry box filled with purified argon. The moisture and oxygen content were less than 1 ppm.

The  $\text{Li-O}_2$  cell was then assembled in a dry glove box (MBraun LABstar) filled with argon using an ECC-Air electrochemical cell (EL-Cell, GmbH) configuration with openings allowing oxygen to inlet and outlet through the cathodic side. Fig. 2 illustrates ECC-Air test cell structure and cell assembly.

### Characterizations of electrolytes

The morphology of the discharge products on cathode was observed by scanning electron microscopy (SEM) (JSM-6060 LV system). The phase constituents of the discharged cathode were investigated by X-ray diffraction (XRD) (Rigaku D/MAX 2000). The diffraction patterns were collected in step scan mode and recorded in  $1^\circ (2\theta)/1 \text{ min}$  between  $10^\circ < 2\theta < 80^\circ$ . The cells were cyclically tested on a MTI Model BST8-MA electrochemical analyzer using  $0.10 \text{ mA/cm}^2$  current density over a voltage range of 2.15–4.25 V and the oxygen gas flow rate was  $15 \text{ ml/s}$ . To investigate the difference in the resistance of the cells before and after the electrochemical cycling test, electrochemical impedance spectroscopy (EIS) measurements were performed from 1000 kHz to 0.1 Hz. Moreover, the electrochemical properties of prepared cells were investigated by carrying out cyclic voltammetry (CV) tests with a scanning rate of  $0.5 \text{ mV s}^{-1}$  between 2.15 and 4.60 V. All electrochemical measurements were carried out at room temperature ( $25^\circ\text{C}$ ).

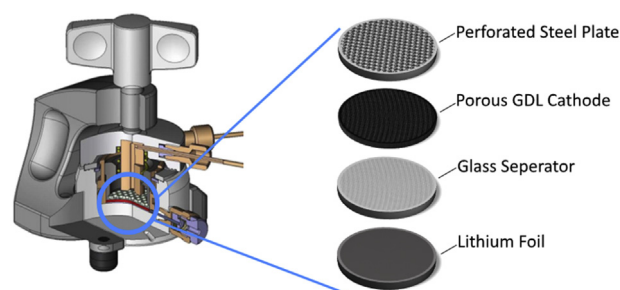


Fig. 2 – ECC  $\text{Li-O}_2$  test cell and cell assembly.

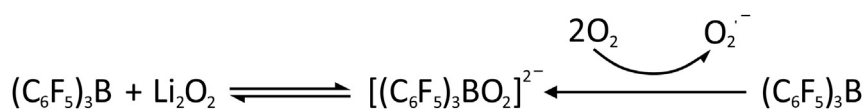


Fig. 1 – Schematic illustration of TPFPB interaction with peroxide anion and superoxide radical anion [15].

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