



# Identifying compatibility of lithium salts with LiFePO<sub>4</sub> cathode using a symmetric cell



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## HIGHLIGHTS

- A symmetric cell (L<sub>0.25</sub>FePO<sub>4</sub>|LiFePO<sub>4</sub>) with sulfimide-based electrolytes is used.
- Capacity fading of the symmetric cell is also scrutinized.
- Li[(FSO<sub>2</sub>)(n-C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>)N]-based electrolyte shows decent compatibility with LiFePO<sub>4</sub>.

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## ABSTRACT

The electrochemical performance of lithium-ion batteries is dominated by the interphase electrochemistry between the electrolyte and electrode materials. A multitude of efforts have been dedicated to the solid electrolyte interphase (SEI) formed on the anode. However, the interphase on the cathode, namely the cathode electrolyte interphase (CEI), is left aside, partially due to the fact that it is hard to single out the CEI considering the complicated anode-cathode inter-talk. Herein, a partially delithiated lithium iron phosphate (Li<sub>0.25</sub>FePO<sub>4</sub>) electrode is used as the anode. Owing to a high voltage plateau ( $\approx 3.45$  V vs. Li/Li<sup>+</sup>), negligible reduction reactions of electrolyte occur on the L<sub>0.25</sub>FePO<sub>4</sub> anode. Therefore, the CEI can be investigated exclusively. Using a LiFePO<sub>4</sub>|Li<sub>0.25</sub>FePO<sub>4</sub> symmetric cell configuration, we scrutinize the compatibility of the electrolytes containing a wide spectrum of lithium salts, Li[(FSO<sub>2</sub>)(C<sub>m</sub>F<sub>2m+1</sub>SO<sub>2</sub>)N] (m = 0, 1, 2, 4), with the LiFePO<sub>4</sub>, in both cycling and calendar tests. It is found that the Li[(FSO<sub>2</sub>)(n-C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>)N] (LiFNFSI)-based electrolyte exhibits the highest compatibility with LiFePO<sub>4</sub>.

## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used as the power source for portable electronic devices for decades, and currently moves to a high gear towards electrification of road transportation. It is well-recognized that the electrolyte plays a key role in LIBs. In today's LIBs, organic carbonate solvent and lithium hexafluorophosphate (LiPF<sub>6</sub>) are employed in combination. The outstanding performance of the LiPF<sub>6</sub>-carbonate electrolytes in LIBs is largely ascribed to its high ionic conductivity, excellent anodic stability and anti-corrosion character against the Al current collector [1]. More importantly, the LiPF<sub>6</sub>-carbonate electrolyte has desirable compatibility with the graphite anode owing to the formation of a high-quality SEI film [1].

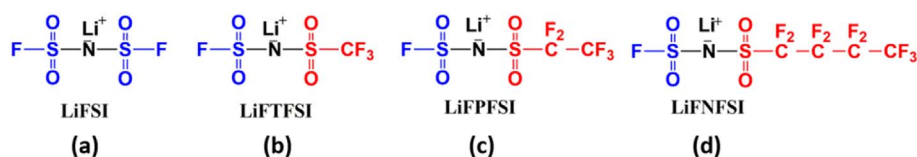
However, LiPF<sub>6</sub>-carbonate electrolytes still suffer from vexing thermal instability and unwanted moisture sensitivity [1–7]. It has been reported that decomposition of LiPF<sub>6</sub>-carbonate electrolyte during battery operation can be initialized by the presence of trace amounts of HF and protic impurities (i.e., H<sub>2</sub>O and alcohols), both of which can cause severe degradation of PF<sub>6</sub><sup>−</sup> anions and carbonate solvents regenerating HF and protic species, particularly at elevated temperatures [7]. Degradation of LiPF<sub>6</sub>-carbonate accelerates the capacity fading of LIBs.

So far, two strategies are employed to tackle the degradation of the LiPF<sub>6</sub>-carbonate electrolytes. One is the introduction of certain additives as a stabilizer to retard the decomposition [8–13]. Nevertheless, this approach only postpones the electrolyte degradation. The other is

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**Scheme 1.** Structures of conducting lithium salts (a) LiFSI, (b) LiFTFSI, (c) LiFPFSI and (d) LiFNFSI.

to develop novel lithium salts to replace LiPF<sub>6</sub>. In past decades, many lithium salts with various kinds of anions have been reported, such as those containing nitrogen [7,14–21], phosphorus [22–24], or boron [25–29] as the central atoms. Among them, sulfonamide-based lithium salts (Li[(FSO<sub>2</sub>)<sub>m</sub>(C<sub>m</sub>F<sub>2m+1</sub>SO<sub>2</sub>)N], *m* = 0, 1, 2, 4, abbr.: LiFSI, LiFTFSI, LiFPFSI, LiFNFSI, respectively, Scheme 1) have attracted unabated attention. These sulfonamide salts-based electrolytes are revealed to have a better electrochemical performance (particularly in terms of cycle life at elevated temperatures) than that containing LiPF<sub>6</sub>, in a wide spectrum of LIB chemistry, including graphite|LiCoO<sub>2</sub>, Li|LiMn<sub>2</sub>O<sub>4</sub>, MCMB|LiMn<sub>2</sub>O<sub>4</sub> and Li|LiFePO<sub>4</sub> [7,16–18]. The improved electrochemical performances are owing to better compatibility of the sulfonamide lithium salt-based electrolyte with the anode (lithium metal and graphite) [7,16–18]. LiFSI-based electrolyte, for example, can form a compact and smooth SEI film on graphite and Li metal surface [19,30–34]. The decent SEI film is formed via decomposition of –FSO<sub>2</sub> groups (i.e., LiF, Li<sub>2</sub>SO<sub>3</sub>, Li<sub>2</sub>SO<sub>4</sub>). However, it remains unknown whether these electrolytes also have good compatibility with the cathode materials.

To understand the compatibility of electrolytes with cathode materials, some factors should be taken into consideration. Current anode materials (i.e., graphite and lithium metal), are unstable towards carbonates used in LIBs [35]. In addition, carbonates decompose at low potentials, ca. 1 V vs. Li/Li<sup>+</sup>, and form SEI films on the graphite anode [1]. Moreover, electrochemical reduction products of electrolyte decomposition may migrate to the cathode. All these make the impact of electrolyte on the cathode ambiguous and difficult to be evaluated exclusively, viz. to be deconvoluted from the anode-cathode coupling. To tackle these problems, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) has been used as the anode owing to the relatively high potential plateaus of 1.55 V vs. Li/Li<sup>+</sup> compared with the graphite [36]. However, the reduction potential of sulfonamide lithium salts (i.e., LiFSI etc.) is ca. 2 V vs. Li/Li<sup>+</sup> [34], much higher than inorganic lithium salts (i.e., LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiAsF<sub>6</sub> etc., reduced at ca. 1 V vs. Li/Li<sup>+</sup> [1]). Therefore, reduction reactions may still occur on the LTO surface when sulfonamide salts are used.

Partially delithiated lithium iron phosphate (Li<sub>x</sub>FePO<sub>4</sub>, 0 < *x* < 1) has been widely used as the counter/reference electrode to investigate oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in aprotic Li–O<sub>2</sub> batteries [37,38]. The outstanding properties include high stability towards oxygen reduced species (i.e., O<sub>2</sub><sup>•−</sup>, LiO<sub>2</sub> and Li<sub>2</sub>O<sub>2</sub>) and organic solvents (i.e., ethers and sulfones) in comparison with the Li metal [37,38]. Moreover, the Li<sub>x</sub>FePO<sub>4</sub> has a high stable potential of ca. 3.45 V vs. Li/Li<sup>+</sup>. Thereby, no reduction reactions, at least theoretically, can occur on the Li<sub>x</sub>FePO<sub>4</sub> surface. By this way, the cathode-electrolyte interactions can be studied exclusively.

Herein, by using a LiFePO<sub>4</sub>|Li<sub>0.25</sub>FePO<sub>4</sub> (LFP|L<sub>0.25</sub>FP) symmetric cell configuration, we report several organic carbonate-based electrolytes containing a spectrum of lithium salts (LiFSI, LiFTFSI, LiFPFSI and LiFNFSI, Scheme 1), and investigate their compatibility with LiFePO<sub>4</sub> cathode in both cycling and calendar aging tests.

## 2. Experimental

### 2.1. General remarks

All the procedures were carried out in an argon-filled glove box (MBraun, both H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm). Li foil (99.999%, China Energy Lithium Co. Ltd.), separator (Celgard 2325). All the conducting

salts: lithium bis(fluorosulfonyl)imide (LiFSI, 99.5%), lithium (fluorosulfonyl) (trifluoromethanesulfonyl)imide (LiFTFSI, 99.5%), lithium (fluorosulfonyl) (pentafluoroethanesulfonyl)imide (LiFPFSI, 99.5%) and lithium (fluorosulfonyl)(nonafluorobutanesulfonyl)imide (LiFNFSI, 99.5%) were received from Suzhou Fluolyte Co., Ltd., China and used without further treatment. Prior to use, ethylene carbonate (EC, battery grade, Aladdin), dimethyl carbonate (DMC, battery grade, Aladdin) were mixed by 1:1 (by volume) and dried with freshly activated 4 Å molecular sieve for at least 48 h.

### 2.2. Preparation of the electrolytes and electrodes

The electrolytes were prepared in an argon-filled glove box (H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm) by dissolving 1.0 M LiX (X = FSI, FTFSI, FPFSI, FNFSI) in a mixture of EC/DMC (1:1, v/v). Water content was less than 20 ppm, as determined by a Mettler-Toledo Karl Fischer titration apparatus (Metrohm KF 831).

The cathode comprised by LiFePO<sub>4</sub> powder: super P: polyvinylidene fluoride (PVDF) = 90:3:7 (by weight) was dispersed in N-methyl-2-pyrrolidinone (NMP), and spread onto stainless steel mesh (Φ12) and then vacuum-dried at 120 °C for 24 h before using. The loading of LiFePO<sub>4</sub> is ca. 3 mg/cm<sup>2</sup>. The stainless steel mesh was used as current collector due to its high chemical stability compared with Al foil [40]. Thus, the impact of conducting salts on LiFePO<sub>4</sub> can be exclusively tackled.

Partially delithiated LiFePO<sub>4</sub> (Li<sub>0.25</sub>FePO<sub>4</sub>) was used as an anode. The detailed setups can be found in literature [39]. In brief, LiFePO<sub>4</sub> was fabricated by mixing active material with Super P (Timcal) and poly(tetrafluoroethylene) (PTFE) binder in a ratio of 8:1:1 (by weight). Afterwards, the Li|LiFePO<sub>4</sub> cells were assembled and charged at a rate of 0.1 C to a point at which ca. 75% active lithium was extracted from the cathode (corresponding to 75% initial capacity). The cycled cells were disassembled in an argon-filled glove box. Then the Li<sub>0.25</sub>FePO<sub>4</sub> electrodes were rinsed with anhydrous DMC and vacuum-dried at room temperature for 3 h. The capacity of Li<sub>0.25</sub>FePO<sub>4</sub> anodes was about in 2 fold excess of the LiFePO<sub>4</sub> cathodes.

### 2.3. Evaluation of Li-ion batteries

The coin-type cells (CR2032) were assembled in an argon-filled glove box using LFP cathode, L<sub>0.25</sub>FP anode, separator (Φ19), and 110 μL electrolyte, respectively. The charge/discharge tests were conducted on a LAND CT2001A battery testing system (Wuhan, China) at a constant current of 0.1C (1 C = 170 mA/g) from −0.7–0.75 V vs. L<sub>0.25</sub>FP (2.75–4.2 V vs. Li/Li<sup>+</sup>) at room temperature. For rate test, the assembled LFP|L<sub>0.25</sub>FP symmetric cells were charged/discharged for five cycles at 0.1/0.1C for conditioning, and were then cycled sequentially at 0.2/0.2, 0.5/0.5, 1/1, 2/2 and 4/4 C at room temperature. The full cell was performed by Biologic VMP3 battery testing system with a T-type Swagelok™ cell, in which, LFP, L<sub>0.25</sub>FP and lithium foil were used as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively.

For the aging test at elevated temperature, these pristine LFP|L<sub>0.25</sub>FP symmetric cells were first cycled for 5 cycles at 0.2/0.2 C at room temperature, following by storage at 60 °C for 7 days in full state-of-charge. Afterwards, the cells were discharged at 0.1 C to investigate the residual capacities at room temperature. Finally, the LFP|L<sub>0.25</sub>FP symmetric cells were charged/discharged for 3 cycles at 0.2/0.2 C. This

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