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Symmetric lithium-ion cell based on lithium vanadium fluorophosphate with ionic liquid electrolyte

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ABSTRACT

Lithium vanadium fluorophosphate, $LiVPO_4F$, was utilized as both cathode and anode for fabrication of a symmetric lithium-ion $LiVPO_4F//LiVPO_4F$ cell. The electrochemical evolution of the $LiVPO_4F//LiVPO_4F$ cell with the commonly used organic electrolyte $LiPF_6$/EC-DMC has shown that this cell works as a secondary battery, but exhibits poor durability at room temperature and absolutely does not work at increased operating temperatures. To improve the performance and safety of this symmetric battery, we substituted a non-flammable ionic liquid (IL) $LiBF_4/EMIBF_4$ electrolyte for the organic electrolyte. The symmetric battery using the IL electrolyte was examined galvanostatically at different rates and operating temperatures within the voltage range of 0.01–2.8 V. It was demonstrated that the IL-based symmetric cell worked as a secondary battery with a Coulombic efficiency of 77% at 0.1 mA cm^{-2} and 25 °C. It was also found that the use of the IL electrolyte instead of the organic one resulted in the general reduction of the first discharge capacity by about 20–25% but provided much more stable behavior and a longer cycle life. Moreover, an increase of the discharge capacity of the IL-based symmetric battery up to 120 mA h g^{-1} was observed when the operating temperature was increased up to 80 °C at 0.1 mA cm^{-2}. The obtained electrochemical behavior of both symmetric batteries was confirmed by complex-impedance measurements at different temperatures and cycling states. The thermal stability of $LiVPO_4F$ with both the IL and organic electrolytes was also examined.

1. Introduction

Recently, room-temperature ionic liquids (RTILs) have come to be considered acceptable media for various chemical and electrochemical applications due to their attractive properties such as wide electrochemical window, good ionic conductivity, high chemical loyalty, negligible vapor pressure and non-flammability. In particular, RTILs, usually called as ILs, have been widely studied as agents for extraction and separation processes, organic syntheses and catalysis, as well as potential electrolytes for energy storage devices and electroplating [1–5]. ILs were first used as electrolytes in lithium-ion batteries more than two decades ago [6]. The main purpose of using them was to address the limitations of conventional organic solvents, especially their flammability, and as a result to improve the batteries' durability and safety, extend their operation temperature ranges, and enhance their power and energy densities. Special interest in different practical applications of ILs has developed ever since the moisture-stable compound 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) was discovered [7]. However, the reduction potentials of $EMIBF_4$ and many similar ILs, some of them are shown in Table 1, are too high to be employed in batteries using Li-metal anodes. One of the most promising ways to avoid the reduction of cations in such ILs is to employ anode materials possessing a higher reduction potential than that of metallic lithium [12]. For instance, the lithiated metal oxides, $Li_4Ti_5O_{12}$ [12] and β-LiAl [13] were employed as anodes in an $EMIBF_4$-based electrolyte. Nevertheless, one of the important problems still to be solved is the discovery of an alternative anode material for an IL-based electrolyte with high reduction potential.

NASICON-type Lithium Vanadium Phosphate $Li_3V_2(PO_4)_3$ has been identified as a useful cathode material for lithium metal and lithium-ion battery applications [14]. In recent studies, monoclinic $Li_3V_2(PO_4)_3$ demonstrated a cathode performance with two plateaus at around 3.8–4.1 and 1.75 V vs. Li/Li$^+$, associated with V^{+4}/V^{+3} and V^{+3}/V^{+2} redox couples, respectively [15–17]. Such properties allow the use of $Li_3V_2(PO_4)_3$ as an anode as well as a cathode. Indeed, quite recently, in our group, this unique ability of $Li_3V_2(PO_4)_3$ was successfully employed in the construction of a symmetric lithium-ion secondary battery, $Li_3V_2(PO_4)_3//Li_3V_2(PO_4)_3$ [15]. The performance of the $Li_3V_2(PO_4)_3$ symmetric battery was examined with an IL electrolyte based on $EMIBF_4$ and, also, an organic electrolyte with EC-DMC (1:1) solvent.

Recently, the structural and lithium insertion properties of lithium vanadium fluorophosphate, $LiVPO_4F$, have been proposed and described in detail by Barkers' group [18–24]. $LiVPO_4F$ has been identified as isostructural with the naturally occurring minerals

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Table 1
Electrochemical windows of various ILs.

ILs	Electrochemical window Cathodic limit, E vs. (Ag/AgCl)/V	Anodic limit, E vs. (Ag/AgCl)/V	Ref.
1-ethyl-3-methylimidazolium fluorohydrogenate, EMI(FH)$_{2.3}$F	−1.7	+1.2	[8]
1-ethyl-3-methylpyrrolidinium fluorohydrogenate, EMP(FH)$_{2.3}$F	−2.3	+3.0	[9]
1-ethyl-3-methylimidazolium hexafluoratantalate, EMITaF$_6$	−2.8	+1.5	[10]
1-ethyl-3-methylimidazolium tetrafluoroborate, EMIBF$_4$	−3.0	+1.4	[11]

travorite, $LiFePO_4 \cdot OH$ [25], and *amblygonite*, $LiAlPO_4$ (OH, F) [26], crystallizing with a triclinic structure (space group $P1$). The $LiVPO_4F$ structure comprises a 3D framework built up from $[PO_4]$ tetrahedra and $[VO_4F_2]$ octahedra with shared oxygen atoms [22,23]. In this framework structure, there are two crystallographic positions within which the lithium ions are statistically distributed [27]. It was reported that $LiVPO_4F$ demonstrated a reversible lithium extraction/insertion reaction based on the V^{3+}/V^{4+} redox couple operating at around 4.2 V vs. Li/Li^+, which is about 0.3 V higher than that for the above-mentioned $Li_3V_2(PO_4)_3$, because of the positive impact of the electronegative fluorine atom on the induction effect of the $PO_4{}^{3-}$ polyanion in the $LiVPO_4F$ structure. More recently, investigations have established an additional lithium insertion reaction at around 1.8 V vs. Li/Li^+ associated with the V^{2+}/V^{3+} redox couple. This allowed the consideration of $LiVPO_4F$ as a potential anode material as well as a cathode. Based on that, it was reported on the fabrication of a symmetric $LiVPO_4F//LiVPO_4F$ lithium-ion battery, in which [1M] $LiPF_6$/EC-DMC (2:1 by weight) was utilized as the electrolyte [21]. Due to their relatively low operating potentials of about 2.4 V, the $Li_3V_2(PO_4)_3$- and $LiVPO_4F$-based symmetric cells can provide only moderate energy density. However, there are clearly advantages from a commercial standpoint, since the as-made lithium-ion cell may be charged in either direction. Furthermore, such symmetric cells should possess good safety characteristics and a low price in a view of the elimination of cost for Li metal. More importantly, since the low redox potentials (compared to the V^{2+}/V^{3+} redox couple) of $Li_3V_2(PO_4)_3$ (−1.25 V vs. Ag^+/Ag) and $LiVPO_4F$ (−1.2 V vs. Ag^+/Ag) lie within the electrochemical window of the ILs shown in the Table 1, these polyanionic compounds might be candidates for alternative anode materials working in combination with an IL-based electrolyte possessing high reduction potential.

In the present study, we report on the fabrication and evaluation of a $LiVPO_4F//LiVPO_4F$ symmetric battery using an IL-based electrolyte. Special attention is paid to improvement of the battery safety by substitution of the commonly used organic electrolyte, $LiPF_6$/EC-DMC, with a non-flammable ionic liquid one, $LiBF_4/EMIBF_4$.

2. Experimental

2.1. Sample preparation

The $LiVPO_4F$ active material was prepared via a two-step synthesis method, described in detail by Barker, Saidi and Swoyer [20], involving vanadium(III) phosphate, VPO_4, as an intermediate phase. The VPO_4 was prepared using the carbothermal reduction (CTR) method [28] based on the $C \rightarrow CO$ carbothermal reaction mechanism, in accordance with the following reaction as:

$$0.5\,V_2O_5 + NH_4H_2PO_4 + C \rightarrow VPO_4 + NH_3 + 1.5\,H_2O + CO \qquad (1)$$

The precursors, V_2O_5 (99.0%, Kanto Chemical Co., Inc., Japan), $NH_4H_2PO_4$ (99.0%, Wako Pure Chemical Industries, Ltd., Japan) and acetylene black (DENKA Co. Ltd., Japan) were finely mixed by ball milling for 4 h at 200 rpm and then pelletized. To enable complete vanadium reduction and to ensure the presence of residual carbon in the product phase, a 25% mass excess of carbon was used over the stoichiometric conditions based on Reaction (1).

An alumina crucible with the precursor mixture was placed into a temperature-controlled tubular furnace and heated up to an ultimate reaction temperature of 750 °C at 2 °C/min heating and cooling rates. The annealing was held for a dwell period of 4 h under a flowing argon atmosphere.

In the second stage of preparation, the obtained VPO_4, which was predominantly black in color (consistent with the presence of residual carbon black), was further reacted with LiF to yield the single-phase $LiVPO_4F$ product

$$LiF + VPO_4 \rightarrow LiVPO_4F \qquad (2)$$

The mixture of LiF and VPO_4 was placed in a quartz tube sealed under a vacuum in order to avoid vanadium oxidation. The Reaction (2) was carried out at 750 °C for a dwell period of 15 min with heating rate of 2 °C/min. After calcination, the tube was quenched by quickly immersing it into a cold bath, to produce $LiVPO_4F$ as a single-phase.

Structural characterization of the synthesized VPO_4 and $LiVPO_4F$ products was carried out by means of powder X-ray diffraction using a Rigaku RINT2100HLR/PC with Cu Kα radiation ($\lambda = 1.54056$ nm) in the 2θ range of 10°–80° with a step of 0.2°.

2.2. Fabrication of the $LiVPO_4F$ symmetric batteries

Electrochemical Li^+ intercalation/extraction was carried out using coin-type cells (type R2032 made from stainless steel SUS316). The symmetric coin cells were assembled using $LiVPO_4F$ as the active materials for both anode and cathode. In order to separate the anodic and cathodic compartments, a polypropylene separator (Celgard 3501) was used. The cathode as well as the anode was fabricated by mixing the active material ($LiVPO_4F$) with acetylene black (AB) and polytetrafluoroethylene (PTFE) binder at a weight ratio of 85:10:5. The mixtures were rolled into a sheet and punched into pellets of about 10 mm in diameter. The pellets were further dried in an oven at 110 °C for 12 h in vacuum. Two types of electrolytes were employed for fabrication of the symmetric cells: organic [1M] $LiPF_6$ in EC-DMC (1:1) (volume ratio) and IL [1M] $LiBF_4$ in $EMIBF_4$. The fabrication of the coin-type cells was carried out in a glove box filled with Ar (moisture and O_2 contents less than 1 ppm).

2.3. Characterization of electrochemical performance of the $LiVPO_4F$ material

The possibility of using the $LiVPO_4F$ material as a cathode as well as anode was estimated by a quasi-open circuit voltage (QOCV) measurement. For the QOCV analysis, conventional metallic lithium half-cell construction was employed at room temperature. The $Li/LiPF_6$/EC-DMC/$LiVPO_4F$ cell was investigated in two different potential ranges: beginning with charging from 2.5 to 5.2 V vs. Li/Li^+ and starting from discharge from 2.5 to 1.3 V vs. Li/Li^+. To minimize the kinetic effects, QOCV measurements were carried out using intermittent charging/discharging [29] of the metallic lithium cells, so-called half-cells, as follows: a current of 0.2 mA cm^{-2} was supplied for 30 min, corresponding to