



A novel dimethyl sulfoxide/1,3-dioxolane based electrolyte for lithium/carbon fluorides batteries with a high discharge voltage plateau



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ABSTRACT

A novel dimethyl sulfoxide/1,3-dioxolane (DMSO/1,3-DO) based electrolyte is proposed for lithium/carbon fluorides (Li/CF_x) batteries to enhance the discharge voltage plateau and energy density. Conductivities of the electrolyte of 1 mol L⁻¹ LiBF₄/DMSO+1,3-DO with different volume ratios are not identical, which have a maximum of 14.85 mS cm⁻¹. From the tests of galvanostatic discharge, the discharge voltage plateau of the Li/CF_x battery with an electrolyte of 1 mol L⁻¹ LiBF₄/DMSO+1,3-DO (5:5, v:v) can reach 2.69 V at 0.1 C, delivering a maximum discharge capacity of 831 mAh g⁻¹ and the highest energy density of 2196 Wh kg⁻¹. Compared to Li/CF_x batteries with an electrolyte of 1 mol L⁻¹ LiBF₄/PC+DME (5:5, v:v), the energy density of Li/CF_x batteries with an electrolyte of 1 mol L⁻¹ LiBF₄/DMSO+1,3-DO (5:5, v:v) has been improved more than 12%. With the help of XRD, SEM, TEM, EIS, FT-IR and GC-MS analysis, the results of this work suggest that DMSO/1,3-DO based electrolyte can significantly improve the discharge performance of Li/CF_x batteries and keep a good electrochemical stability during discharge. The main reason for improvement of discharge performance is decreasing of both the overpotential of electrochemical polarization of CF_x cathodes during discharge and the overpotential of ohmic polarization by increasing the ion conductivity of electrolyte.

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1. Introduction

Li/CF_x cells are known to have the highest theoretical specific capacity when compared to other primary lithium batteries, such as Li/SOCl₂ and Li/MnO₂ batteries [1,2]. These batteries with high energy density are being developed for military, spacial and medical applications, such as soldier portable power sources, space long term exploratory missions and implantable medical devices [3,4]. Theoretically, a CF_x with x=1 has a high specific capacity of 865 mAh g⁻¹, about twice that of SOCl₂ currently used in primary Li/SOCl₂ batteries [5]. In most non-aqueous liquid electrolyte, CF_x (x=1) cathode has an open circuit potential of 3.2–3.5 V (vs. Li/Li⁺) [6]. However, the discharge voltage plateau of a real Li/CF_x cell (x=1) (~2.5 V) is much lower than this value, showing significant polarization [7]. The reasons for this high polarization are mostly related to the low electronic conductivity of CF_x materials and to the slow kinetics of cell reactions [8].

In previous reports, much effort has been focused on the improvement of CF_x materials. These efforts include the study of various preparation methods of CF_x materials, construction of highly conductive collector and surface modification of CF_x cathodes [9–17]. Besides the CF_x materials, it is noteworthy that the electrolyte is another key factor on discharge performance of Li/CF_x batteries [18,19]. It is well known that the electrolyte requires high ionic conductivity, low melting point, high boiling point, and good electrochemical stability for high-performance batteries [20,21]. It is also well known that the electrolyte of Li/CF_x cells is composed of a lithium salt and an organic solvent blend. Conventional lithium salts contain LiBF₄ [22], LiPF₆ [23], LiAsF₆ [4], and LiClO₄ [24]. The solvents are the mixture of some organic solutions, which include carbonate solvents (EC, PC, DMC, EMC) and ether reagents (DEC, TEE) [25–28]. Recently, some new solvents as a component of electrolyte have been developed to further improve the discharge performance of Li/CF_x batteries. G. Nagasubramanian et al. reported a chemical approach to improve the discharge performance of Li/CF_x cells by adding an ABA{Tris(1,1,1,3,3,3-hexafluoroisopropyl) borate} additive in the electrolyte of Li/CF_x batteries [23]. They found that the ABA additive may dissolve the LiF from the plugging pores on cathode surface and

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keep the bulk of cathode accessible for further discharge reaction. S.S. Zhang et al. used a mixed solution of acetonitrile (AN) and γ -butyrolactone (BL) as the solvent of low temperature electrolyte for high energy density Li/CF_x batteries. They found that the use of AN/BL electrolyte (0.5 mol L⁻¹ LiBF₄, 1:1 AN/BL) in Li/CF_x cells can improve the power capability and low temperature performance [29]. E. Rangasamy et al. reported a high energy density Li/CF_x cell with a solid bifunctional electrolyte of Li₃PS₄. The bifunctional electrolyte of Li₃PS₄ may reconcile both inert and active characteristics through a synergistic discharge mechanism of CF_x and Li₃PS₄ [18]. In order to further improve the discharge performance, it is necessary to develop more new electrolyte of Li/CF_x batteries. Unfortunately, the study on improvement of the electrolyte of Li/CF_x batteries has not been paid enough attention until now.

The electrolyte of Li/CF_x batteries should satisfy many requirements, i.e. ionic conductivity, volatility, viscosity, electrochemical stability and safety [30]. Dimethyl sulfoxide (DMSO), as a highly polar versatile solvent, has favorable advantages, including high dielectric constant (46.68, at 298 K), large dipole moment (4.3 Debye at 298 K) and low volatility (B.P. 189.1°C). Especially, DMSO exhibits a high salt solubility to produce well-conducting solutions with a wide electrochemical window in non-aqueous batteries [31]. However, it is highly desirable but still unexplored to investigate the electrochemical behaviors of DMSO-based electrolyte in Li/CF_x batteries. Owing to the high viscosity (1.948 cP), DMSO is commonly used as the electrolyte mixed with other low viscosity solvents [32]. 1,3-dioxolane (1,3-DO), as a cyclic ether with low dielectric constant and low viscosity, has been commonly used as a solvent of non-aqueous electrolyte [33]. In this study, the DMSO/1,3-DO solution as a mixed solvent of electrolyte for Li/CF_x batteries was prepared and characterized. Both ionic conductivities and viscosities of the electrolyte of 1 mol L⁻¹ LiBF₄/DMSO+1,3-DO with different volume ratios of solvents have been investigated. Moreover, the discharge behavior of Li/CF_x batteries with DMSO/1,3-DO based electrolyte is also studied. It is noteworthy that the electrolyte of 1 mol L⁻¹ LiBF₄/DMSO+1, 3-DO (v:v, 5:5) can enhance the discharge voltage plateau and energy density of Li/CF_x batteries evidently.

2. Experimental

CF_x (x=0.99–1.08, Daikin Corp Japan) was used as the cathode material. LiBF₄ (Battery grade) was obtained from Guotai-Huarong Co.Ltd (China). Dimethyl sulfoxide (DMSO), 1,3-dioxolane (1,3-DO), propylene carbonate (PC), 1,3-dimethoxy ethane (DME) and other organic solvents (battery grade) were purchased from Aladdin and used without further treatment.

2.1. Preparation of the electrolyte

The electrolyte was prepared in an argon-filled glove box (Mikrouna Advanced 1440/750, H₂O<0.1 ppm, O₂<0.1 ppm). DMSO and 1,3-DO solvents were mixed with different volume ratios, and then LiBF₄ was dissolved in the mixed solution. Similarly, LiBF₄/PC+DME (5:5,v:v) solution was prepared as the

control electrolyte. Compositions of the five electrolyte samples, which contain the DMSO/1,3-DO based and the PC/DME based solutions, are listed in Table 1. The concentration of LiBF₄ salt in every sample is the same, which is 1.0 mol L⁻¹.

2.2. Preparation of Li/CF_x batteries

The electrode film of cathode was mixed by 85 wt% CF_x, 9 wt% Super P (M.M.M. Carbon Inc, Belgium) and 6 wt% LA133 aqueous binder (Chengdu Indigo, Co. Ltd, A acrylonitrile copolymer aqueous dispersion) in the distilled water. Then, the obtained slurry (~0.4 mm thick) was coated onto an aluminum foil current collector. The coating was dried in an 110 °C-oven for 12 h, and the resulting electrode film was cut into small disks with a diameter of 16 mm for coin cell testing. The electrode disks were further dried at 110 °C under vacuum for 24 h, and then transferred into a glove-box for cell assembly. Each electrode contains around 8 mg of active materials. Li/CF_x coin cells (CR2430) were assembled by using Celgard® 3500 membrane as the separator. A lithium foil (20mm diameter) was used as the anode.

2.3. Characterization

The ionic conductivity of electrolyte was measured by using a conductometer (Mettler Toledo SevenExcellence™, Switzerland) in an argon-filled glove box. Ionic conductivity constant was determined with a standard KCl solution (0.01 mol L⁻¹). The measurements were repeated for three times, and the average value was given. The viscosity of electrolyte was tested by a cone-plate viscometer (Brookfield, LVDV-III+CP). Coin cells were discharged on a Land Cell tester (CT2001A, Wuhan Jinnuo Electronics Company, China) and the cut-off voltage was set at 1.5 V. The electrochemical stability of electrolyte was tested on a simulated cell by using both Fourier transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-MS) analytical methods before/after discharge (at 0.1 C). The FT-IR spectra were tested by a thermo-model Nicolet 6700 spectrometer. The combined instrument of GC-MS is Agilent Technologies 7890A/5975C. A HP-5MS capillary column (30 m×0.32 mm×0.25 mm) was used for separation, and a helium gas (99.99%) was used as the carrier gas (constant flow rate: 1 mL min⁻¹). X-ray diffraction (XRD) patterns of CF_x cathodes were measured by a Rigaku D/max-2500 diffractometer with a Cu K α radiation in the 2 θ range of 20°–80°. The surface morphologies of CF_x cathodes were observed by a Hitachi S-4800 scanning electron microscopy (SEM). The grain size of LiF were investigated by a transmission electron microscope (TEM, JEM-2100F). Electrochemical impedance spectroscopy (EIS) of a two-electrode electrochemical cell was performed by using a Solartron Instruments Model 1400/1470E. A frequency range from 100 kHz to 0.01 Hz with an AC oscillation of 10 mV was used. All tests were performed at 25 °C.

3. Results and discussion

The electrochemical properties of electrolyte were firstly investigated. Both viscosities and conductivities of five electrolyte samples were shown in Table 2 and Table 3, respectively. The viscosities of DMSO/1,3-DO based electrolyte increase with decreasing the content of 1,3-DO, indicating that 1,3-DO may dilute the mixed solution effectively. Moreover, the ion conductivity of sample C is the highest among the five samples. The appearance of the maximum is generally explained by the synergetic effect of DMSO and 1,3-DO on ionic conductivity of the solution, which comes from the high solvating power of DMSO and the low viscosity of 1,3-DO [34].

Table 1
Compositions of five electrolyte samples (Concentration of electrolyte: 1 mol L⁻¹)

Sample	Lithium salt	Solvent	Solvent volume ratio
A	LiBF ₄	DMSO/1, 3-DO	1:9
B	LiBF ₄	DMSO/1, 3-DO	3:7
C	LiBF ₄	DMSO/1, 3-DO	5:5
D	LiBF ₄	DMSO/1, 3-DO	7:3
E	LiBF ₄	PC/DME	5:5

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