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Electrochemical performance and kinetics of LiFePO₄/C cathode in a low-temperature electrolyteJingwen Yao^{1,3}, Feng Wu^{2,3*}, Borong Wu^{2,3}, Xinping Qiu¹, Chunwei Yang^{2,3}, and Ning Li^{2,3}¹ Department of Chemistry, Tsinghua University, Beijing 100084, China² School of Chemical Engineering & the Environment, Beijing Institute of Technology, Beijing 100081, China³ National Development Center of High Technology Green Materials, Beijing 100081, China

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Abstract

The electrochemical performance of LiFePO₄/C cathode in a carbonate-based electrolyte (1.0M LiPF₆/ EC-DMC-PC-FEC) was tested in coin type cells at low temperatures. The discharge capacities of the LiFePO₄/C cathode were about 161.6mAh/g (20°C), 141.4mAh/g (-10°C) and 112.9mAh/g (-20°C) at 0.1C charge-discharge rate. The electrode kinetics of LiFePO₄/C cathode was determined at different temperatures using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The analyses demonstrate that the sluggish of charge-transfer reaction on the LiFePO₄/C-electrolyte interface and the dramatic decrease in lithium ion diffusivity in the bulk LiFePO₄/C material were the key performance limiting factors at low temperature.

Keywords: LiFePO₄/C cathode, Lithium ion batteries, Low-temperature electrolyte, Fluoroethylene carbonate

1 Introduction

Lithium-ion batteries may often be used in low-temperature environment, especially as power sources of electric or electric-hybrid vehicles. LiFePO₄ is the most promising cathode material for large-scale lithium ion batteries because of its safety and low cost [1-5]. Nevertheless, low-temperature performance is still challenging requirement for this material. Ma et al. [6] investigated the low-temperature performance of LiFePO₄/C cathode in a quaternary carbonate-based electrolyte (1.0 M LiPF₆ / EC+DMC+DEC+EMC (1:1:1:3, v/v)). It can be found that the discharge capacities of the LiFePO₄/C cathode were about 134.5mAh/g (20°C), 114mAh/g (0°C), 90mAh/g (-20°C) and 69mAh/g (-40°C) at 1C rate by using this new electrolyte. Zhang et al. [7] studied the low-

temperature performance of LiFePO₄/C material in a 1.0M (0.9LiBF₄-0.1LiBOB)/EC+PC+EMC (1:1:3, v/v) electrolyte. The discharge capacities of the LiFePO₄/C | Li cell were over 75mAh/g at -30°C and over 45mAh/g at -50°C using a 1C charge-discharge rate. Fluoroethylene carbonate (FEC) has been very positively considered as an electrolyte additive to form a stable SEI layer in lithium secondary batteries [8-10]. McMillan et al. [8] demonstrated the effect of FEC as an electrolyte additive for graphite/LiCoO₂ cells at room temperature and found that SEI layer can be formed from the decomposition of FEC on the graphite surface. Ryou et al. [9] reported that FEC can function as a good additive of electrolyte to significantly improve the capacity retention of

LiMn₂O₄/graphite Li-ion cells at high temperature at 60°C. However, there are few publications describing the electrochemical performances of cathodes in high FEC-content electrolytes at low temperatures.

This study presents an investigation of the electrochemical properties of LiFePO₄/C cathode in a carbonate-based electrolyte (1.0M LiPF₆ / EC-DMC-PC-FEC) at low temperatures. Cyclic voltammetry and electrochemical impedance spectroscopy were used to study the electrode kinetics of the cathode.

2 Experimental

The LiFePO₄/C cathode was prepared using 80% LiFePO₄/C powder that was synthesized by solid-state reaction, 10% acetylene black and 10% polyvinylidene fluoride (PVDF), incorporated into a CR2025 coin type cell with a lithium foil counter electrode and 1.0M LiPF₆/EC-DMC-PC-FEC electrolyte. The 1.0M LiPF₆ / EC-DMC (EC:DMC=1:1, v/v) electrolyte was used as a reference. The charge-discharge performance was examined using CT2001A Land instrument from 2.5 to 4.2V. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted by a CHI660a analyzer.

3 Results and discussion

Figure 1 compares the charge-discharge profiles of the LiFePO₄/C cathode with two different electrolytes at various operation temperatures at 0.1C. It is clear that the reversible capacity decreases remarkably as the operation temperature decreases. Compared with a capacity of 150.9mAh/g (20°C) and 87mAh/g (-20°C) using binary electrolyte, the LiFePO₄/C cathode with 1.0M LiPF₆ / EC-DMC-PC-FEC low-temperature electrolyte delivers much higher reversible discharge capacity of 161.6mAh/g (20°C), 150.1mAh/g (0°C), 141.4mAh/g (-10°C) and 112.9mAh/g (-20°C), and the low-temperature capacity retention is as high as 92.9%, 87.5% and 69.9%, respectively. Furthermore, as the operation temperature falls, the charge voltage increases and the discharge voltage decreases slightly. The charge and discharge plateaus at 20°C are 3.45-3.40V ($\Delta V = 0.05$ V) for low-temperature electrolyte and 3.47-3.40V ($\Delta V = 0.07$ V) for binary electrolyte, respectively. When the temperature decreases down to -20°C, the voltage plateaus are 3.50-3.36V ($\Delta V = 0.14$ V) for low-temperature electrolyte, whereas

ΔV is as high as 0.23V for binary electrolyte. It indicates that the polarization behavior of the LiFePO₄/C cathode is weakened effectively by using the low-temperature electrolyte.

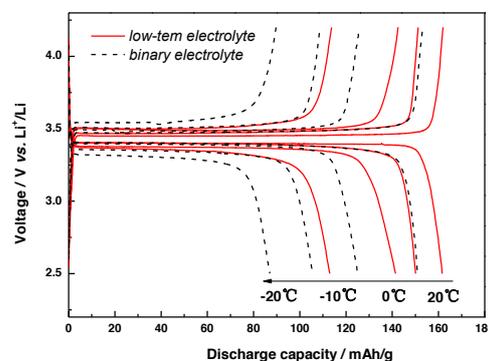


Figure 1: Charge-discharge profiles of the LiFePO₄/C cathode with different electrolytes under various operation temperatures at 0.1C(17mA/g) rate.

Figure 2 compares the rate performance of the LiFePO₄/C cathode with the low-temperature electrolyte at 20°C and -10°C. It can be seen, the LiFePO₄/C cathode presents 80.6% (130.2mAh/g) of the 0.1C capacity (161.6mAh/g) at 1C, and 54.8% (88.5mAh/g) up to 10C rate at 20°C. But the rate performance is obviously hindered at -10°C, only 54.3% (87.8mAh/g) and 33.3% (47.1mAh/g) are obtained at 1C and 5C, respectively. The charge-discharge characteristics of LiFePO₄/C cathode show that the operation temperature has a pronounced effect on rate performance of electrode.

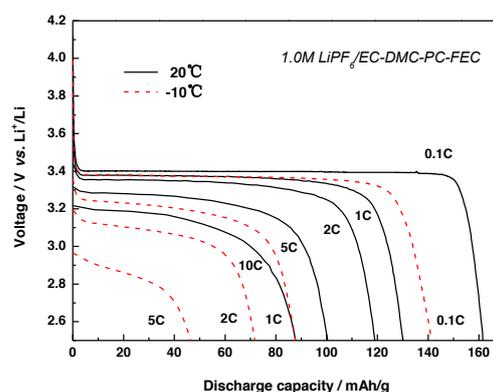


Figure 2: The rate performance of LiFePO₄/C cathode with low-temperature electrolyte at 20°C and -10°C. Specific charge current was 17mA/g at 0.1C rate.

The cyclic voltammetry was operated on the LiFePO₄/C cathode with the low-temperature electrolyte at 0.1mV/s between 2.5V and 4.5V under different temperatures (Figure 3). It is obvious that as the temperature decreases, the potential separation between the cathodic and

anodic peaks increases obviously, furthermore, the peak intensity decreases and the peaks are broadened. It indicates that the reversible insertion of lithium in the LiFePO₄/C cathode is hindered at lower temperature due to sluggish kinetics, especially when operation temperature falls to -20°C.

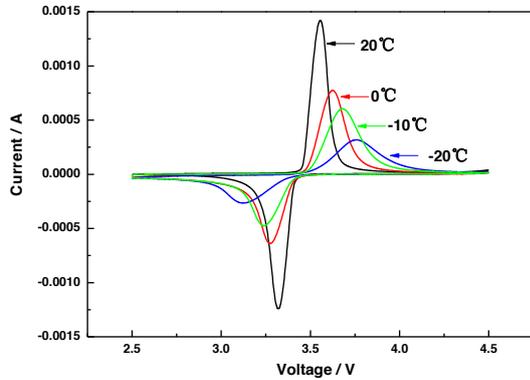


Figure 3: Cyclic voltammograms of LiFePO₄/C cathode under various temperatures between 2.5 and 4.5V at a scan rate of 0.1mV/s.

The EIS measurement of LiFePO₄/C cathode with the low-temperature electrolyte was carried out in the frequency range from 10 mHz to 100 kHz with an ac voltage signal of ±5 mV. Figure 4 shows that the Nyquist plot in the open circuit state with fully discharged LiFePO₄/C cathode under various temperatures. It can be seen obviously, each Nyquist plot is composed of one semicircle in the high frequency region and a straight line in the low frequency region. The intercept of the high frequency semicircle with the real impedance axis *Z'* identifies the ionic conductivity of the electrolyte (*Re*). The high-frequency semicircle is attributed to the charge-transfer reaction resistance (*Rct*) in the LiFePO₄/C cathode-electrolyte interface. The straight line in the low frequency region is related to Warburg impedance (*Zw*) that is associated with Li⁺ diffusion through the LiFePO₄/C cathode. The equivalent circuit used to fit the Nyquist plots shows in Figure 5 [11], the derived impedance parameters *Re* and *Rct* at different temperatures were listed in Table 1.

The lithium diffusion coefficient in LiFePO₄/C cathode can be calculated using the following exp (1) [11]:

$$D_{Li} = \frac{R^2 T^2}{2n^4 F^4 C_{Li}^2 \sigma^2} \quad (1)$$

σ is the Warburg factor which has the relationship with *Z'*:

$$Z' = Re + Rct + \sigma \omega^{-1/2} \quad (2)$$

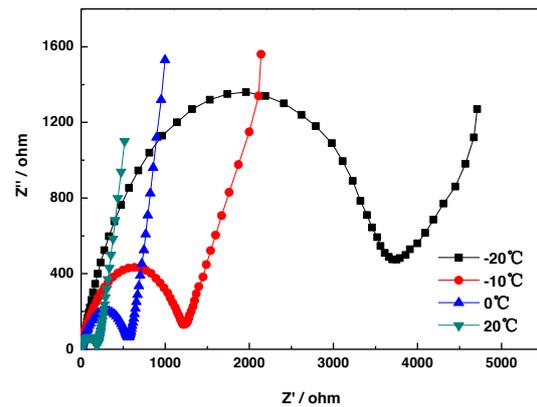


Figure 4: EIS of the LiFePO₄/C cathode (fully discharged) under various temperatures.

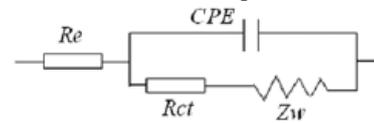


Figure 5: Equivalent circuit model used for EIS fitting of the LiFePO₄/C electrode.

The graph of *Z'* against $\omega^{-1/2}$ in the low frequency region is a straight line with the slope of σ . The *Z'*- $\omega^{-1/2}$ plots of different temperatures were presented in Figure 6. The diffusion coefficient calculated using above exp (1) was also listed in Table 1.

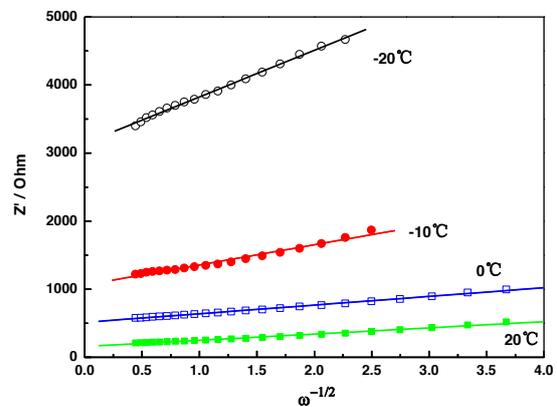


Figure 6: Graph of *Z'* plotted against $\omega^{-1/2}$ at low frequency region for LiFePO₄/C cathode (fully discharged) at various temperatures.

It was found that the ohmic resistance (*Re*) increased gradually as the temperature decreased. Nevertheless, the decrease of temperature showed much more pronounced effect on the charge-transfer reaction in the electrode-electrolyte interface and Li-ion diffusion capacity through the LiFePO₄/C cathode, furthermore, a sharp change took place as the temperature fell down to -20°C,

the charge-transfer resistance (R_{ct}) remarkably increased to 3661Ω and the lithium diffusion coefficient (D_{Li}) decreased to $3.73 \times 10^{-14} \text{ cm}^2/\text{S}$ at -20°C .

Table 1: Impedance parameters derived using equivalent circuit model and lithium diffusion coefficient D_{Li} for LiFePO_4/C cathode (fully discharged).

T(°C)	R_e (Ω)	R_{ct} (Ω)	D_{Li} (cm^2/s)
20	1.61	145.6	2.82×10^{-12}
0	1.89	462.4	1.25×10^{-12}
-10	2.09	1047	2.14×10^{-13}
-20	2.82	3661	3.73×10^{-14}

4 Conclusions

The low-temperature performance of LiFePO_4/C cathode in a carbonate-based electrolyte (1.0M $\text{LiPF}_6/\text{EC-DMC-PC-FEC}$) was studied. The LiFePO_4/C cathode presents a discharge capacity of 161.6mAh/g (20°C), 141.4mAh/g (-10°C) and 112.9mAh/g (-20°C) at 0.1C rate, respectively, but the rate performance is obviously hindered as the operation temperature falls. CV and EIS measurements demonstrate clearly that the increase of charge-transfer reaction resistance in the LiFePO_4/C -electrolyte interface and decrease of lithium-ion diffusion capability in the bulk LiFePO_4/C material are the main limiting aspects at low-temperature.

Acknowledgments

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Jingwen Yao received her PhD degree from Beijing Institute of Technology at 2007. Her research interests include nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode, LiFePO_4 cathode to investigate their particle size / morphology–property relationships using different synthesis methods, and also development of new layered transition metal oxide cathodes with high energy capacity. Dr Yao is currently a post doctor at Department of Chemistry in Tsinghua University.

