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Wang, G
Kang, H
Chen, M
et al.

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Influence of electrolytes on the low-temperature performance of LiFePO₄/C composite electrodes

Guixin Wang^{1,*}, Hanchang Kang¹, Miao Chen¹, Kangping Yan¹, Xueshan Hu², Elton J. Cairns^{3,4}

¹ College of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China

² BASF Battery Materials (Suzhou) Co., Ltd., Suzhou Industrial Park, Suzhou 215123, Jiangsu, China

³ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA, USA,

⁴ Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

ABSTRACT

The electrolyte, a key cell component for the successful operation of electrode materials, is greatly affected by its solvents. The influence of nonaqueous solvents on the electrochemical performance of a LiFePO₄/C composite cathode was investigated at various operating temperatures. The kinetics of the LiFePO₄/C composite electrode reaction, including changes of rate capability, redox potential, polarization degree, electrode reaction process, lithium ion diffusion efficiencies, exchange current densities, and activation energies, were evaluated using various techniques. The composition and composition ratio of solvents greatly affect the electrode reaction kinetics. In the mixed solvents of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC), EMC is beneficial for the room temperature performance, while the substitution of 20 vol.% of EMC by ethyl acetate (EA) is good for the low temperature performance. When 30 vol.% of DMC is substituted by 10

* Corresponding author.
E-mail address: guixin66@scu.edu.cn, guixinwang1@gmail.com
Tel.: +86-28-85406192.

vol.% of EMC and 20 vol.% of EA, the diffusion coefficient of lithium ions increases from 2.62×10^{-12} to $2.50 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, while the exchange current density increases from 2.20×10^{-5} to $3.75 \times 10^{-5} \text{ A cm}^{-2}$ at -20°C , and the activation energy of the electrode reaction decreases from 48.36 to 33.01 kJ mol^{-1} . These results are significant for the exploration of appropriate electrolytes for the extensive applications of LiFePO_4/C composite electrodes.

KEYWORDS: Electrolyte; Solvent effect; LiFePO_4/C ; Electrochemical performance; Electrode kinetics

1. INTRODUCTION

The serious environmental problems encourage the use of (hybrid) electric vehicles in cities, and energy materials are necessary for the vehicle power sources operating at different ambient temperatures. Among various positive electrode materials, olivine-structured LiFePO_4 has attracted considerable interest because of its unique structure, good thermal stability, plentiful raw material supply, and environmental compatibility¹, but the low-temperature performance must be improved for its practical application in different environments²⁻⁶. Low-temperature cell performance is strongly influenced by electrolyte composition, electrode material composition and battery structure. Current studies on the enhancement of the low-temperature performance of LiFePO_4 focus on doping elements⁷, carbon coating^{8,9}, or using quaternary electrolytes with specific formulations^{3,10}.

As the blood of batteries, the electrolyte will affect the transport properties of Li^+ ions¹¹⁻¹³ as well as the solid interface film on the electrodes, and the solvent plays an important role in determining cell performance¹³. The solvent affects the transfer processes of mass, heat, momentum, and charge by forming different solvated ions and altering the physical properties of the electrolyte, such as the melting point, viscosity, solubility, and conductivity. Many solvents, including EC, DMC, EMC and EA, have been employed to enhance the performance of Li ion cells for different applications. Among these solvents, EC is frequently used because it is aprotic, polar, and non-volatile¹³⁻¹⁸; DMC can improve the solubility and conductivity of the electrolyte because of its relatively higher dielectric

constant and low viscosity^{13, 15}; EMC is a useful co-solvent to widen the liquid range and to enhance the conductive behavior of the EC-based electrolytes^{13, 17-21}; and EA can improve ionic transport properties in a solution^{13, 22, 23}. The solvent mixture is of great significance for improving the electrochemical performance of electrolytes. A ternary electrolyte of 1.0 M LiPF₆/EC + DMC+ EMC (1: 1: 1) is reported to enhance the low-temperature performance of LiCoO₂²⁴, and a quaternary electrolyte of LiPF₆/EC + DEC + DMC + EMC is found to improve the low-temperature performance of LiNi_{0.8}Co_{0.2}O₂²⁵. However, the influence of the type and combination of solvents on the low-temperature performance of LiFePO₄ is still unclear, which is not beneficial for its extensive application.

Herein, three types of LiPF₆ electrolytes containing different solvents were chosen and compared for improving the electrochemical performance of LiFePO₄/C composite electrodes using various techniques at different cell operating temperatures. The electrode reaction process was analyzed, and the functions of the various solvents were discussed, which is important for the compatibility of electrode materials and electrolytes.

2. EXPERIMENTAL

2.1 Materials

In order to decrease the cost and realize sustainable development, a LiFePO₄/C composite was

synthesized with a facile route by using $\text{Fe}_{1.5}\text{P}$ waste slag from the industrial production of yellow phosphorus²⁶. Three types of electrolytes containing different solvents, denoted as “1”, “2” and “3”, were provided by BASF Battery Materials (Suzhou) Co., Ltd. These electrolytes are all composed of 1.0 M LiPF_6 and 2 wt.% of vinylene carbonate (VC) additive, along with different solvents like EC, DMC, EMC and EA, and the detailed compositions are shown in Table 1. The key physicochemical properties of each solvent are summarized in Table 2. Electrolytes “1” and “2” are ternary systems of EC+DMC+EMC with different ratios of DMC and EMC, while electrolyte “3” is a quaternary system with part of the EMC substituted by EA to decrease the melting point and increase the conductivity of the electrolyte.

2.2 Characterization

The phase structures of the synthesized sample were identified by X-ray diffraction (XRD, Philips X'Pert Pro, Netherlands) with a step of $0.04^\circ/\text{s}$ within the 2θ range from 10° to 70° using $\text{Cu K}\alpha$ radiation at a power of $40\text{ kV}\times 100\text{ mA}$. The morphology and the particle size were observed using a field-emission scanning electron microscope (FESEM, JSM-7500F, Japan). The carbon content was determined by a carbon-sulfur analyzer (CS-902, China).

2.3 Electrochemical evaluation

The electrochemical measurements were conducted on CR2032 coin cells at different temperatures. The cathodes were composed of 80 wt.% of the as-synthesized LiFePO_4/C powder, 15 wt.% of

conductive acetylene black and 5 wt.% of commercial LA-132 binder (Chengdu Indigo Power Sources Co. Ltd, China). Lithium metal was used as the anode, acting as the counter and reference electrode. Using the above various electrolytes, cells were assembled by sandwiching a Celgard 2300 microporous separator between the cathode and the anode in a glove box filled with dry argon gas^{26, 27}.

The electrochemical performance of the cells was evaluated via galvanostatic charge/discharge curves, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The galvanostatic charge/discharge tests were performed in a potential range of 2.4 ~ 4.2 V versus Li^+/Li on a Neware battery-testing instrument (Shenzhen Neware Technology Ltd., China). CV and EIS measurements were carried out on an electrochemical station including a PAR 273A potentiostat/galvanostat and a signal recovery model 5210 lock-in-amplifier controlled by Powersuite software (Princeton Applied Research, USA). The potential window for the CVs is the same for the above galvanostatic tests. As for the EIS measurements, the AC signal amplitude is 10 mV, and the frequency range is between 100 kHz and 0.01 Hz. The lithium ion diffusion coefficient (D_{Li}) is calculated according to the function of the impedance and the square root of frequency in the low frequency region of the EIS data. According to the exchange current density at different temperatures, the activation energies of the Li^+ electrode reaction are calculated by using the Arrhenius equation.

3. RESULTS AND DISCUSSION

3.1 Phase structure and morphological analysis

After being well mixed by ball milling, the precursor was preheated at 500 ~ 550 °C in air, and then calcined at ~700 °C in argon²⁶. Finally, a black product was obtained and ground for further analysis. According to the carbon-sulfur analysis, the carbon content is about 5 wt.%. In order to determine the composition and phase structure, powder XRD was conducted. From the XRD pattern in Figure 1, all the indexed peaks match well with the standard peaks of LiFePO₄ (JPCDS card number 40-1499), indicating the product is olivine LiFePO₄ with an orthorhombic structure and a Pmnb space group. The absence of impurity peaks indicates that the purity of the product is high. Via Rietveld refinement, the lattice parameters along the axes of a, b, and c are 0.60, 1.04 and 0.47 nm, respectively, and the cell volume is 0.29 nm³. Among the indexed peaks, four main peaks centered at $2\theta \approx 20.8^\circ$, 25.5° , 29.7° , and 35.5° , can be attributed to the (011), (111), (121), and (131) crystal planes of LiFePO₄, respectively. The average crystallite size is 46.6 nm by calculating from these main planes using Scherrer's formula²⁷.

The SEM images in Figure 2 show that the as-synthesized LiFePO₄/C composite consists of many small quasi-spherical particles. Part of these particles agglomerate to form larger ones, while some small particles distribute among and on the surface of some large particles. The small particle size is in the the range of 15 to 30 nm, and the agglomeration size can reach 200 nm.

3.2 Charge/discharge performance

Typical galvanostatic charge/discharge curves of the CR2032 lithium cells using various electrolytes at the 0.1 C rate at different temperatures are shown in Figure 3. The composition and ratio of solvents greatly affect the charge/discharge behavior of LiFePO₄/C composite under the same conditions. Some key parameters, including discharge capacity, columbic efficiency (η), intermediate voltage difference between the charge and discharge plateaus (ΔV), are summarized in Table 3. As temperature decreases from 20 °C to -20 °C, the charge/discharge plateaus become shorter, the capacity declines, and the ΔV increases, indicating that the overvoltage increases at low temperatures. Electrolytes “1” and “2” without EA deliver better performance than electrolyte “3” containing EA at 20 °C, which is in contrast

to the results at 0 or -20 °C. Electrolyte “2” and electrolyte “3” exhibits the highest discharge capacity and the lowest ΔV at 20 °C and -20 °C, respectively, suggesting that the internal resistance of the cell using electrolyte “3” is the lowest at low temperature. Furthermore, electrolyte “3” is superior to electrolytes “1” and “2” in enhancing the columbic efficiency at -20 °C, indicating that electrolyte “3” with the quaternary solvent mixture provides good capacity reversibility at low temperatures. Considering the composition and the electrochemical performance, EA is inferior to EMC for enhancing the performance at room temperature, but EA is superior to EMC at low temperatures. On the other hand, electrolytes “1” and “2” contain the same components except with different ratios between the solvents of EMC and DMC, but their performances differ greatly. Electrolyte “2” with a higher content of EMC extends the low temperature operation range, and is better than electrolyte “1” for enhancing the discharge capacity at both room temperature and low temperature, indicating that EMC is superior to DMC for improving the electrochemical performance of LiFePO_4/C composite over a wide temperature range. The difference in discharge capacity may be mainly due to the different freezing points of EMC (-55 °C) and DMC (4.6 °C) which will affect the diffusion of lithium ions ¹³. Electrolytes “2” and “3” contain the same ratio of EC and DMC except the different contents of EMC and EA. Electrolyte “2” with 0 vol.% of EA and 50 vol.% of EMC exhibits better performance than Electrolyte “3” with 20 vol.% of EA and 30 vol.% of EMC at 20 °C. However, Electrolyte “2” exhibits poorer performance than Electrolyte “3” in enhancing the discharge capacity at low temperatures of 0 °C or -20 °C, indicating that EMC is superior to EA for enhancing the electrochemical performance of the LiFePO_4/C composite at room temperature, but EMC is inferior to EA for improving the low-temperature performance.

Figure 4 shows the differential capacity plots of the data shown in Figure 3, which reflects the changes of potential dE with reaction time dt because of the constant current charge/discharge. They all have an obvious pair of symmetric anodic/cathodic peaks at various temperatures, indicating that the

reversibility of the oxidation/reduction process is high. When the temperature is at -20 °C, the curves of the cell using Electrolyte "3" exhibit two pairs of small extra oxidation/reduction peaks ($\sim 4.2/2.8$ V and $\sim 3.8/3.1$ V) besides the pair of obvious redox peaks ($\sim 3.5/3.4$ V). However, these extra peaks disappear when the temperature increases to 0 °C or 20 °C. Noticeably, no other extra peaks appear in the curves of electrolytes "1" and "2" at any temperature. Considering the extra redox peaks and improved discharge capacity of the LiFePO_4/C composite at -20 °C, EA in the electrolyte may take part in the electrode reaction to enhance the low temperature performance.

Figure 5 shows the rate performance of the LiFePO_4/C composite at various temperatures as the rate ranges from 0.1 to 1.0 C. It can be seen that the rate capability declines with the decrease of temperature. At 20 °C, Electrolyte "2" has the best rate performance, and the discharge capacities can reach 144.9, 119.6, and 94.5 mAh g^{-1} when the rates are 0.1 C, 0.5 C, and 1.0 C, respectively. At 0 °C, Electrolyte "2" also has the best rate performance, and the discharge capacities are 98.9, 83.9, and 73.4 mAh g^{-1} when the rates are 0.1 C, 0.5 C, and 1.0 C, respectively. However, when the temperature is decreased to -20 °C, Electrolyte "3" has the best rate performance, and the discharge capacities can reach 86.0, 61.1, and 52.0 mAh g^{-1} when the rates are 0.1 C, 0.5 C, and 1.0 C, respectively.

3.3 Voltammetric analysis

Figure 6 shows the cyclic voltammograms of the cells using different electrolytes with a scanning rate of 0.2 mV s^{-1} at -20 °C. They all have a pair of obvious redox peaks, but the peak positions and

intensities differ greatly. The values of oxidization potential (E_O), reduction potential (E_R), potential difference between oxidization and reduction peaks (ΔE), oxidation peak current (I_O) and reduction peak current (I_R) are summarized in Table 4. The oxidization peak at ~ 3.75 V and the reduction peak at ~ 3.20 V correspond to the de-intercalation of Li^+ ions from LiFePO_4 and the intercalation of Li^+ ions into FePO_4 , respectively. The electrolyte sequence for increasing values of ΔE of the cells is “1” > “2” > “3”, indicating that the polarization of the cell using Electrolyte “3” is the lowest at -20 °C. Meanwhile, the electrolyte sequence for increasing values of I_O and I_R is “3” > “2” > “1”, suggesting that electrolyte “3” has a higher electrochemical reaction activity than electrolyte “1” or “2” at -20 °C. These results, consistent with the above galvanostatic charge/discharge results, further confirm that EA is better than EMC and DMC for enhancing the electrochemical performance of the LiFePO_4/C composite at -20 °C.

3.4 Impedance analysis

To investigate the electrode reaction kinetics and diffusion behavior of lithium ions using different electrolytes, EIS measurements were conducted under the same conditions with an open circuit potential of 3.44 V by charging at different temperatures. The Nyquist plots of the LiFePO_4/C composite using different electrolytes, along with the equivalent circuit used for EIS data modeling are presented in Figure 7. Their shapes are similar, and all curves consist of a depressed semicircle in the high-to-medium frequency region and an oblique line in the low frequency region, suggesting a similar electrode reaction process. However, the impedance values are greatly affected by the electrolytes with different solvents. The intercept of the curve on the real axis in the high-frequency region is attributed to the ohmic resistance of the electrolyte, and the depressed semicircle in the high-to-medium

frequency range is related to the complex reaction process over the interface between electrode and electrolyte, including electrolyte film and charge transfer impedances ²⁸. The inclined line in the low frequency range is associated with the Warburg impedance, which is from the semi-infinite diffusion of Li^+ ions in the bulk electrode ^{26,28}.

The EIS curves are well fitted with the $R(QR)(Q(RW))$ model provided in Figure 7(d). Considering the inhomogeneities such as porosity, roughness and geometry in the electrode system, a constant phase element (CPE) Q is used to substitute for capacitance, and its value is determined by frequency independent parameters related to temperature ²⁹. In the circuit, R_s , R_f , Q_f , R_{ct} , W , and Q_d correspond to the ohmic resistance of the electrolyte, the resistance of the electrolyte film, the CPE of the film, the charge transfer reaction resistance, the Warburg impedance, and the CPE of the electrolyte film/electrode interface, respectively. In order to make clear the function of solvents for the electrode reaction process, the fitting results of R_s , R_{ct} and R_f by using ZsimpWin and Z-view software are summarized in Table 5. The values of R_s , R_{ct} and R_f increase gradually as temperature decreases. When the temperature is at 20 °C, the resistance sequence of the electrolytes is “1” < “3” < “2”, the resistance sequence of charge transfer is “1” < “2” < “3”, and the resistance sequence of the electrolyte film is “3” < “2” < “1”, indicating that EMC with higher content reduces the conductivity of electrolyte, but EMC and EA disturb the electrode reaction process. When the temperature decreases to 0 or -20 °C, the resistance sequence of the electrolytes is “1” < “2” < “3”, and the resistance sequence of the electrolyte film is “3” < “1” < “2”, but the resistance sequences of charge transfer are “1” < “3” < “2” and “3” < “2” < “1”, respectively. These results show that DMC is beneficial for improving the electrolyte conductivity at room temperature and low temperatures, and EA is good for the charge transfer reaction and for decreasing the electrolyte film resistance at low temperatures, but EMC will hinder the charge transfer and increase the electrolyte film resistance at low temperatures.

The chemical diffusion coefficients of lithium ions D_{Li^+} ($\text{cm}^2 \text{s}^{-1}$) are calculated from the complex

plane using the following equations of (1) and (2) according to the Fick's law ^{30, 31}.

$$Z_w = \sigma(1-i)\omega^{-1/2} \quad (1)$$

$$D_{Li^+}^{1/2} = \frac{RT}{2^{1/2} n^2 F^2 A \sigma C_{Li^+}} \quad (2)$$

Where, Z_w is Warburg impedance at low frequency, σ is the Warburg coefficient, $i = \sqrt{-1}$, ω is the frequency, R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the working temperature (K), n is the number of transferred electrons, F is the Faraday constant ($F = 96500 \text{ C mol}^{-1}$), and A is the active surface area, and C_{Li^+} (mol cm^{-3}) is the molar concentration of lithium ions in an electrode active material. According to Equation (1), the Warburg coefficient σ can be obtained from the slope of impedance versus square root of frequency in the Warburg section. Figure 8 exhibits the dependence of impedance Z' on square root of low frequencies at various temperatures, and the values of σ are summarized in Table 5. According to Equation (2), the chemical diffusion coefficients D_{Li^+} ($\text{cm}^2 \text{ s}^{-1}$) using various electrolytes are compared in Figure 9. Under the same conditions, the different values of D_{Li^+} are from the different electrolytes. At 20 °C, the electrolyte sequence for increasing values of D_{Li^+} is “1” < “3” < “2”, but the sequence changes to “1” < “2” < “3” at low temperatures of 0 or -20 °C, indicating the sequence for enhancing the diffusivity of lithium ions is DMC < EA < EMC at room

temperature, while the sequence changes to DMC < EMC < EA at low temperatures.

To further evaluate the intrinsic rates of electron transfer between electrolyte and electrode at various temperatures, the exchange current density (j) was calculated using the above charge transfer resistance R_{ct} obtained from the modeling results of EIS data by the following formula ³².

$$j = \frac{RT}{nFR_{ct}A} \quad (3)$$

Where, the meanings of parameters like R , T , n , F , A , are consistent with those in the Equations (1) and (2). To confirm more clearly the temperature effect on the electrode reaction, the apparent activation energy (E_a) of the electrode reaction was calculated using the conventional Arrhenius equation ³³

$$\ln j = \ln K - \frac{E_a}{RT} \quad (4)$$

Where, K is a temperature-independent coefficient. The formula is further transformed to the following one according to different temperatures T_1 and T_2 .

$$\ln \frac{j_2}{j_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

The exchange current densities of j at various temperatures and the average activation energy E_a obtained from the three temperatures are summarized in Table 6. According to the results, DMC is good for the electron transfer at 20 or 0 °C, while EMC or EA does well for the electron transfer at -20 °C. On the other hand, Electrolyte “1” with highest content of DMC and lowest content of EMC has the

highest J , while Electrolytes “2” and “3” with a higher content of EMC have a lower E_a , indicating that EMC is superior to DMC to improve the extraction/insertion of lithium ions in the electrode reaction. Furthermore, Electrolyte “3” with EA replacing some of the EMC has a slightly lower activation energy than Electrolyte “2”, which is indicative of an easier electrode reaction.

According to the composition and structure of the different solvents in the electrolytes, the performance differences are due to the different solvents. EC has good properties for forming a Solid/Electrolyte Interface (SEI) film and dissolving lithium salts, while VC is an ideal additive for forming a film to enhance capacity and cycling performance, which are reasons for the addition of 30 vol.% of EC and 2 wt.% of VC to each electrolyte. Thus, other solvents and matching ratios are key factors for affecting the electrochemical performance of electrode materials at various temperatures. Based on the above analytical results and the physicochemical properties of the different solvents, EMC is better than DMC for improving the discharge capacity and rate performance of the LiFePO_4/C composite at various temperatures of 20, 0 and $-20\text{ }^\circ\text{C}$. In addition, EMC is superior to EA for improving the discharge capacity and rate performance at room temperature, but EMC is inferior to EA for enhancing the electrochemical performance at low temperatures of 0 and $-20\text{ }^\circ\text{C}$. Consequently, the combination and content of solvents are significant for improving the electrochemical performance of the LiFePO_4/C composite electrode material at different temperatures.

4. CONCLUSIONS

The type and ratio of solvents in a 1.0 M LiPF_6 electrolyte affect greatly the electrochemical performance of a LiFePO_4/C composite active material at different temperatures. The influence of the solvents on the electrode reaction kinetics has been discussed in detail. According to the experimental results using various techniques, EMC is superior to DMC for improving the electrochemical performance of a LiFePO_4/C composite at 20, 0 and -20°C , and EMC is better than EA for increasing the electrochemical performance at room temperature, but EMC is inferior to EA for enhancing the electrochemical performance at low temperatures of 0 and -20°C . On the other hand, DMC is beneficial for improving the electrolyte conductivity at room temperature or low temperatures, EA is good for the electrode reaction and for decreasing the electrolyte film resistance at low temperatures, and EMC will enhance the charge transfer and increase the SEI film resistance at low temperatures. The sequence for enhancing the diffusivity of lithium ions is $\text{DMC} < \text{EA} < \text{EMC}$ at 20°C , while the sequence changes to $\text{DMC} < \text{EMC} < \text{EA}$ at low temperatures of 0 and -20°C . The activation energies of the electrode reaction using electrolytes “1”, “2” and “3” were calculated to be 48.36, 33.29 and 33.01 kJ mol^{-1} , respectively, indicating that the ability for improving the extraction/insertion of lithium ions is $\text{DMC} < \text{EMC} < \text{EA}$. The combination of EC: DMC: EMC (30: 20: 50 in volume) was demonstrated to enhance the room temperature performance, while the combination of EC: DMC: EMC: EA (30:20:30:20 in volume) is beneficial to the low temperature performance. The experimental

results are of great significance for exploring appropriate electrolytes using combined solvents for improving the electrochemical performance of the LiFePO_4/C composite to satisfy possible applications at different temperatures.

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Table Captions

Table 1. Compositions of various electrolytes.

Table 2. Physical properties of selected aprotic solvents at 25 °C.

Table 3. Discharge capacities (mAh g^{-1}), η (%), and ΔV (V) of LiFePO_4/C composite at 0.1 C using different electrolytes under various temperatures.

Table 4. E_O , E_R , ΔE , I_O and I_R of LiFePO_4/C composite using different electrolytes at -20 °C.

Table 5. R_s , R_{ct} and R_f of LiFePO_4/C composite using different electrolytes under various temperatures.

Table 6. σ , D_{Li} , j and E_a of LiFePO_4/C composite using different electrolytes under various temperatures.

Tables

Table 1. Compositions of various electrolytes.

Electrolyte *	EC : DMC : EMC: EA (Volume ratio)
“1”	30:50:20:0
“2”	30:20:50:0
“3”	30:20:30:20

* All contain 2 wt.% VC.

Table 2. Physical properties of selected aprotic solvents at 25 °C.

Solvent	EC	DMC	EMC	EA	VC
Structure	22	/	C	22	22
Viscosity (10^{-3} Pa·s)	1.93 (40 °C)	0.59	0.65	0.46	1.9 (40 °C)
Dielectric constant, ϵ	89.60	3.10	2.40	6.02	96
Melting point (°C)	39	4.60	-55	-84.00	22
Boiling point (°C)	248	90	108	71.10	162
Flash point (°C)	160	18	26.7	-3	73
Density (g cm^{-3})	1.32 (39 °C)	1.06	1.01	0.89	1.36
Dipole moment (debye)	4.61	0.76	0.89	--	--
Donor number	16.40	15.10	--	17.10	--

Table 3. Discharge capacities (mAh g^{-1}), η (%), and ΔV (V) of LiFePO_4/C composite at 0.1 C using different electrolytes under various temperatures.

Electrolyte	20 °C			0 °C			-20 °C		
	Capacity	η	ΔV	Capacity	η	ΔV	Capacity	η	ΔV
“1”	140.4	99.4	0.065	96.2	98.0	0.07	77.5	91.4	0.15
“2”	144.9	99.8	0.051	98.9	100	0.17	78.4	95.0	0.17
“3”	131.8	97.8	0.056	99.4	97.5	0.14	86.0	99.2	0.10

Table 4. E_o , E_R , ΔE , I_o and I_R of LiFePO_4/C composite using different electrolytes at $-20\text{ }^\circ\text{C}$.

Electrolyte	$E_o(\text{V})$	$E_R(\text{V})$	$\Delta E(\text{V})$	$I_o(\text{mA cm}^{-2})$	$I_R(\text{mA cm}^{-2})$
“1”	3.75	3.15	0.60	0.48	-0.42
“2”	3.79	3.20	0.59	0.63	-0.50
“3”	3.74	3.21	0.53	0.71	-0.56

Table 5. R_s , R_{ct} and R_f of LiFePO_4/C composite using different electrolytes under various temperatures.

Electrolyt	20°C			0°C			-20°C		
	$R_s(\text{ohm})$	$R_{ct}(\text{ohm})$	$R_f(\text{ohm})$	$R_s(\text{ohm})$	$R_{ct}(\text{ohm})$	$R_f(\text{ohm})$	$R_s(\text{ohm})$	$R_{ct}(\text{ohm})$	$R_f(\text{ohm})$
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“1”	1.4	45.7	3.6	4.3	270.0	4.2	6.4	874.7	28.7
“2”	2.2	71.4	6.9	11.0	306.2	15.5	11.6	560.8	30.4
“3”	1.6	73.3	2.6	13.1	297.2	3.1	13.6	513.2	18.5

Table 6. σ , D_{Li} , j and E_a of LiFePO_4/C composite using different electrolytes under various temperatures.

Electrolyte	Temperature (°C)	σ	D_{Li} ($\text{cm}^2 \text{s}^{-1}$)	J (A cm^{-2})	E_a (kJ mol^{-1})
“1”	20	9.58	2.88×10^{-10}	4.48×10^{-4}	48.36
	0	22.76	4.41×10^{-11}	7.76×10^{-5}	
	-20	87.35	2.62×10^{-12}	2.20×10^{-5}	
“2”	20	9.05	3.22×10^{-10}	3.13×10^{-4}	33.29
	0	22.76	4.42×10^{-11}	6.79×10^{-5}	
	-20	80.10	3.11×10^{-12}	3.80×10^{-5}	
“3”	20	9.25	3.12×10^{-10}	3.04×10^{-4}	33.01
	0	17.03	6.88×10^{-11}	7.00×10^{-5}	
	-20	28.26	2.50×10^{-11}	3.75×10^{-5}	

Figure Captions

Figure 1. XRD pattern of the as-synthesized LiFePO_4/C composite.

Figure 2. SEM images of the as-synthesized LiFePO_4/C composite.

Figure 3. Galvanostatic charge/discharge curves of LiFePO_4/C composite using different electrolytes under various temperatures.

Figure 4. Differential capacity plots of the data shown in Figure 3.

Figure 5. Influence of electrolyte on the rate performance of LiFePO_4/C composite under different temperatures.

Figure 6. Cyclic voltammograms of LiFePO_4/C composite using various electrolytes at $-20\text{ }^\circ\text{C}$.

Figure 7. Nyquist plots of LiFePO_4/C composite under different temperatures with various electrolytes (a) “1”, (b) “2”, (c) “3”, and (d) corresponding equivalent circuit.

Figure 8. Z' vs. $\omega^{-1/2}$ of LiFePO_4/C composite with various electrolytes under different temperatures.

Figure 9. Influence of temperature and electrolyte on the chemical diffusion coefficient of lithium ions.

Figures

Figure 1. XRD pattern of the as-synthesized LiFePO₄/C composite.

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Figure 2. SEM images of the as-synthesized LiFePO_4/C composite.

Figure 3. Galvanostatic charge/discharge curves of LiFePO₄/C composite using various electrolytes under different temperatures.

Figure 4. Differential capacity plots of the data shown in Fig. 2.

Figure 5. Influence of electrolyte on the rate performance of LiFePO_4/C composite under different temperatures.

Figure 6. Cyclic voltammograms of LiFePO_4/C composite using various electrolytes at -20°C .

Figure 7. Nyquist plots of LiFePO_4/C composite under different temperatures using various electrolytes

(a) “1”, (b) “2”, (c) “3”, and (d) corresponding equivalent circuit. The experiment data are shown in

open circle, and the fitting data are shown in black line.

Figure 8. Z' vs. $\omega^{-1/2}$ of LiFePO_4/C composite using various electrolytes under different temperatures.

Figure 9. Influence of temperature and electrolyte on the chemical diffusion coefficient of lithium ions.