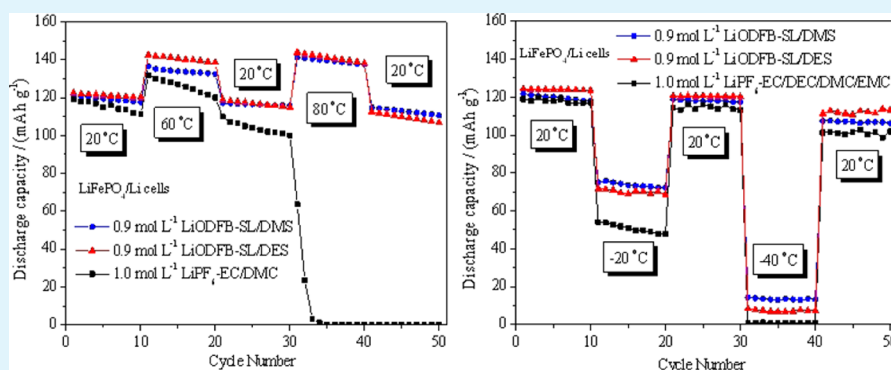


Studies on Electrochemical Performances of Novel Electrolytes for Wide-Temperature-Range Lithium-Ion Batteries

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ABSTRACT: Wide-temperature electrochemical behaviors of sulfolane (SL) with lithium difluoro(oxalato)borate (LiODFB) are studied using dimethyl sulfite (DMS) and diethyl sulfite (DES) as mixed solvents, respectively. In LiFePO₄/Li cells, LiODFB-SL/DMS and LiODFB-SL/DES electrolytes always exert several advantages over a wide temperature range, such as stable cycling performance and good rate performance. Besides, in Li/mesophase carbon microbead cells, these novel electrolytes respectively exhibit excellent film-forming characteristics at both +60 and -20 °C, such as the formation of a stable and conductive SEI layer. It suggests that LiODFB-SL/DMS and LiODFB-SL/DES electrolytes are alternative candidate electrolytes for wide-temperature-range lithium-ion batteries.

KEYWORDS: lithium-ion battery, lithium difluoro(oxalato)borate, sulfolane, wide-temperature electrolyte, high-temperature batteries, low-temperature batteries

1. INTRODUCTION

Electrolytes used in commercial lithium-ion batteries are composed of LiPF₆ dissolved in organic carbonates, whose properties are crucial for lithium-ion batteries with a wide operating temperature range. Earlier research in the area of electrolytes has resulted in the development of a system consisting of 1.0 mol L⁻¹ LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, by volume, the same below), which has been demonstrated to have better performance at high temperature than most of the other LiPF₆-based electrolytes.¹ However, LiPF₆ has poor thermal stability to decompose to LiF and PF₅ at elevated temperatures, and the latter readily hydrolyzes to form HF and PF₃O.² Both products of the hydrolysis reaction are highly reactive to both negative and positive electrodes. Besides, the low melting point (36.4 °C) of EC usually leads to poorly conductive solutions at low temperature.³ To address these issues, a 1.0 mol L⁻¹ LiPF₆-EC/diethyl carbonate (DEC)/DMC/ethyl methyl carbonate (EMC) (1:1:1:3) electrolyte formulation has been suggested as a suitable electrolyte for improving the low-temperature performance of lithium-ion batteries.⁴ However, low-EC-

content electrolyte systems have certain negative influence in terms of their electrode film-forming characteristics, which will further destroy the high-temperature performance of an anode solid electrolyte interphase (SEI) layer.⁵ For these reasons, searches for alternative salts and solvents for lithium-ion batteries that are capable of operating over a wide temperature range have received increasing attention lately.

Studies have shown that when the salt of LiPF₆ is replaced with LiBF₄ and lithium bis(oxalato)borate (LiBOB), electrolytes would have better low- and high-temperature performances, respectively.^{6,7} However, neither of those salts could achieve a sufficiently good performance for wide-temperature-range operation because of the limited solubility, negative effects on electrodes, and other disadvantages for varied and complicated reasons.

Lithium difluoro(oxalato)borate (LiODFB), containing the same molecular moieties as those of LiBOB and LiBF₄, has the

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combined advantages of LiBOB and LiBF₄.⁸ Like LiBOB, LiODFB also has good thermal stability, which is very necessary for high-temperature performance. In addition to that, in contrast to LiBOB, the low-temperature performance of LiODFB is improved because of the higher solubility and lower content of the oxalate group in its molecule. First, the higher solubility is essential to reduce the viscosity and increase the wettability of the electrolyte. Second, the lower content of the oxalate group results in less irreversible capacity in the initial cycle. Third, LiODFB greatly facilitates formation of the SEI film on the surface of the carbon anode material, at the same time significantly reducing the impedance. For all of these reasons, LiODFB is considered to be a prospective salt for wide-temperature-range lithium-ion batteries.

However, we encountered a bottleneck in terms of solvents of the LiODFB-based electrolyte by reference to the composition of the LiPF₆-based electrolyte such as an EC/DMC mixed system. It was found that the impedance of the SEI layer with the LiODFB-based electrolyte was below that of the LiBOB-based electrolyte, but it was still higher than that of the LiPF₆-based electrolyte.⁹ Therefore, how to exert LiODFB's excellent electrochemical properties by selecting suitable solvents is a key before its application in lithium-ion batteries.

Linear sulfites, such as dimethyl sulfite (DMS) and diethyl sulfite (DES), are excellent cosolvents for improving low- and high-temperature performances because of their low melting points (−141 and −112 °C, respectively), low viscosities (0.87 and 0.83 mPa s, respectively), and high boiling points (126 and 159 °C, respectively).^{10,11} Sulfolane (SL) is a common solvent known to show high dielectric constant (43.3), boiling point (285 °C), and flash point (166 °C).^{11,12} Our previous research found that the impedance of the SEI layer with LiBOB-SL/DMS and LiBOB-SL/DES electrolytes was far below that of the layer with LiPF₆-EC/DMC electrolyte because of sulfur-containing compounds in the SEI layer, which are better conductors for Li⁺ ions than analogical carbonates.^{11,13} This is very attractive for the low-temperature performance of lithium-ion batteries. More than that, the preferred electrolyte, LiBOB-SL/DMS, exhibits excellent film-forming characteristics, good thermal stability, and good electrochemical performance at elevated temperature such as 60 °C.

Thus, combining many advantages of LiODFB salts with those of SL/DMS and SL/DES solvents, LiODFB-SL/DMS and LiODFB-SL/DES may be alternative electrolytes for wide-temperature-range operation. We report these two kinds of novel electrolytes based on that above. In order to effectively evaluate the wide-temperature-range properties, the high-temperature performances of these novel LiODFB-based electrolytes are compared with that of a 1.0 mol L^{−1} LiPF₆-EC/DMC (1:1) system and the low-temperature performances of these novel LiODFB-based electrolytes are compared with that of a 1.0 mol L^{−1} LiPF₆-EC/DEC/DMC/EMC (1:1:1:3) system.

2. EXPERIMENTAL SECTION

LiODFB was synthesized in our laboratory with an improved method,⁹ and the purity exceeded 99.5%. Synthetic methods of organic sulfites DMS and DES were referenced from the literature.¹⁴ SL was purchased from Liaoyang Guanghua Chemical Co., Ltd. (0.4 nm molecular sieve), and alkali metals were used to dry all kinds of solvents at least 2 days until the moisture content was usually less than 20 ppm as measured by Karl Fischer titration.

As frames of reference, 1.0 mol L^{−1} LiPF₆-EC/DMC (1:1) and 1.0 mol L^{−1} LiPF₆-EC/DEC/DMC/EMC(1:1:1:3) systems were pur-

chased from Chaoyang Yongheng Chemical Co., Ltd. Electrolytes 0.9 mol L^{−1} LiODFB-SL/DMS (1:1) and 0.9 mol L^{−1} LiODFB-SL/DES (1:1), which were used as two kinds of novel electrolytes, were prepared in a glovebox.

LiFePO₄ was purchased from Hunan Shanshan Advanced Material Co., Ltd., and a mesophase carbon microbead (MCMB) was obtained from Fangda Carbon New Material Co., Ltd. The positive electrode was prepared with a mixture of 84 wt % LiFePO₄ (29.4 mg), 8 wt % poly(vinylidene fluoride) (PVDF; 2.8 mg), and 8 wt % carbon black (2.8 mg), coated on aluminum foil. The negative electrode was composed of 92 wt % MCMB (23.0 mg) and 8 wt % PVDF (2.0 mg), coated on copper foil.

A CHI660C electrochemical analyzer (Shanghai, China) was employed to measure electrochemical impedance spectroscopy (EIS) spectra of the negative and positive electrodes (in two-electrode cells: negative and positive electrodes as work electrodes and lithium sheets as counter electrodes). For Li/MCMB and LiFePO₄/Li half-cells, the impedance measurements were tested at the fully lithiated state of 0.01 V and completely delithiated state of 4.2 V, respectively. A 5 mV sinusoidal alternating-current (ac) disturbance was applicable to each electrode from the 100 kHz to 10 mHz frequency range.

Experimental cells (2030 type, diameter of 20 mm, and thickness of 3.0 mm) are assembled in an argon-atmosphere glovebox using lithium sheets as anodes and the above-mentioned electrodes and electrolytes as cathodes and electrolytes, respectively. Celgard (2400) porous polypropylene was employed as separators. Electrochemical measurements of the cells were carried out on a LAND CT2001A tester (Wuhan, China) in the different voltage ranges of 0.01–2 V for Li/MCMB cells and 2.7–4.2 V for LiFePO₄/Li cells. Charging and discharging performances of the cells in different conditions were tested under the same conditions.

3. RESULTS AND DISCUSSION

3.1. Charge–Discharge Curves of LiFePO₄/Li Cells.

Parts a and b of Figure 1 show the initial charge–discharge curves of LiFePO₄/Li cells using different electrolytes with 0.5 C of discharge rate at +60 and −20 °C, respectively. It can be observed that every LiODFB-based cell shows an obvious charge–discharge plateau and a small difference value of the charge–discharge voltage. At 60 °C, when cells containing LiODFB-based electrolytes are compared those with the LiPF₆-EC/DMC electrolyte, the following trend is observed in increasing difference value of the charge–discharge voltage: LiODFB-SL/DMS (0.06 V) < LiODFB-SL/DES (0.12 V) < LiPF₆-EC/DMC (about 0.3 V). With a decrease of the temperature, the difference value increases because of an increase of the polarization potential. At −20 °C, the difference values of the charge–discharge voltage of the cell with LiODFB-SL/DMS and LiODFB-SL/DES electrolytes are found to be 0.34 and 0.32 V, which are still much smaller than that of the cell with the LiPF₆-EC/DEC/DMC/EMC electrolyte (about 0.78 V). The results indicate that cells containing LiODFB-based electrolytes have smaller polarization potential and better cycle performance than cells with LiPF₆-based electrolytes.

With coherence to the polarization resistance, the cells using LiODFB-SL/DMS and LiODFB-SL/DES electrolytes have higher discharge voltage plateaus than those using the LiPF₆-based electrolyte. As shown in Figure 1a, discharge voltage plateaus are 3.39 V for the LiODFB-SL/DMS electrolyte, 3.36 V for the LiODFB-SL/DES electrolyte, and 3.25 V for the LiPF₆-EC/DMC electrolyte at 60 °C. With a decrease of the temperature, the discharge voltage plateau decreases. At −20 °C, the discharge voltage plateaus are 3.24 and 3.23 V for two kinds of LiODFB-based electrolytes and 2.81 V for the LiPF₆-EC/DEC/DMC/EMC electrolyte, as shown in Figure 1b. This

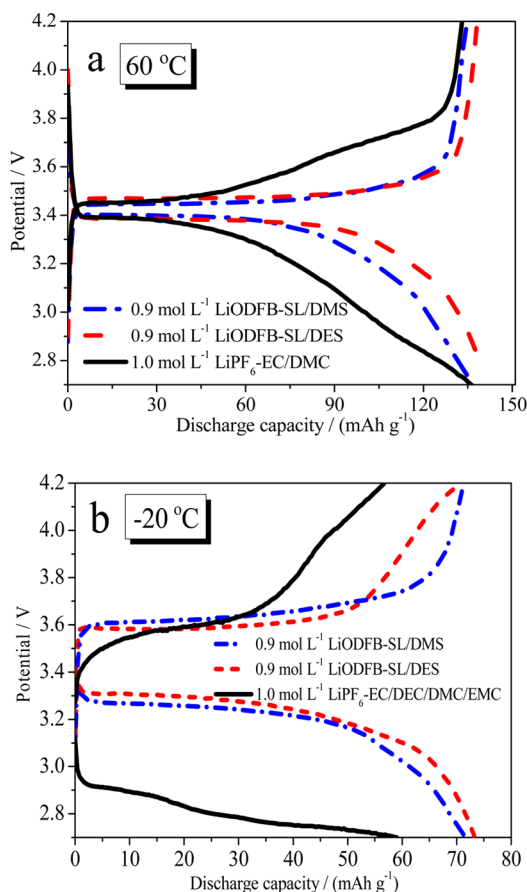


Figure 1. Initial charge–discharge curves of $\text{LiFePO}_4/\text{Li}$ cells with different electrolytes, operated (a) at $+60\text{ }^\circ\text{C}$ and (b) at $-20\text{ }^\circ\text{C}$. The discharge rate is 0.5 C .

indicates that cells with two kinds of novel electrolytes have higher working voltage and can run longer under a normal working voltage at wide temperature.

3.2. Cycling Performances of $\text{LiFePO}_4/\text{Li}$ Cells. Recent research demonstrates that lithium-ion battery capacity loss in circulation is mainly caused by cyclable lithium loss owing to lithium-consuming SEI layer growth and the rate capability loss as a result of the rise of interfacial resistance.¹⁵ Parts a and b of Figure 2 show the cycling performances of $\text{LiFePO}_4/\text{Li}$ half-cells using different electrolytes with 0.5 C of discharge rate at $+60$ and $-20\text{ }^\circ\text{C}$, respectively. As shown in Figure 2a, cells with both LiODFB-based electrolytes show much lower capacity fading than the one with the $\text{LiPF}_6\text{-EC/DMC}$ electrolyte at $60\text{ }^\circ\text{C}$. After 200 cycles, capacity retention efficiencies of cells with LiODFB-SL/DMS, LiODFB-SL/DES, and $\text{LiPF}_6\text{-EC/DMC}$ electrolytes are found to be 89.11%, 83.27%, and 11.18%, respectively. As we expected, the results show that LiODFB-based electrolytes have better thermal stability than LiPF_6 -based electrolytes. Besides, after 50 cycles at $-20\text{ }^\circ\text{C}$, when the cells containing LiODFB-based electrolytes are compared with the baseline formulation of the $\text{LiPF}_6\text{-EC/DEC/DMC/EMC}$ electrolyte, the following trend is observed in decreasing capacity retention efficiency: LiODFB-SL/DMS (94.57%) > LiODFB-SL/DES (87.24%) > $\text{LiPF}_6\text{-EC/DEC/DMC/EMC}$ (46.03%), as shown in Figure 2b. The results indicate that LiODFB-SL/DMS and LiODFB-SL/DES electrolytes have a positive effect on wide-temperature-range cycling performances.

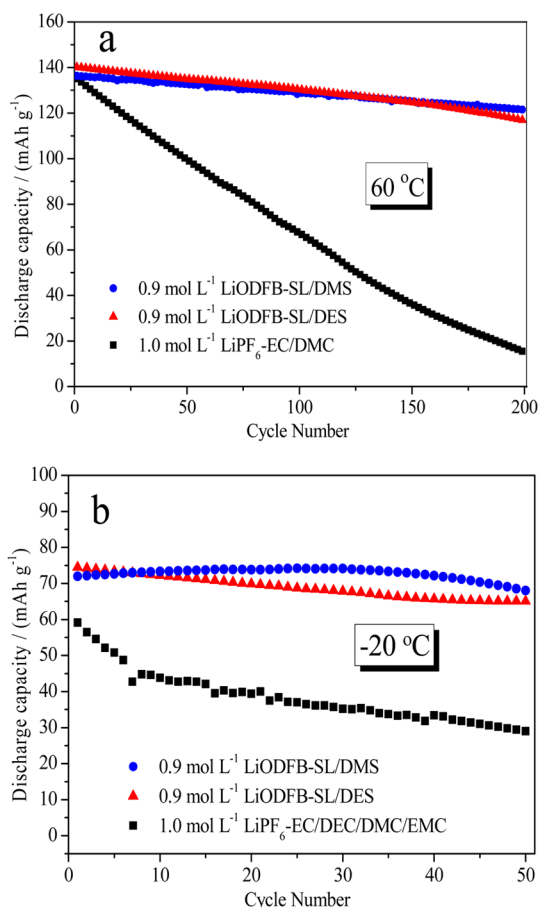


Figure 2. Discharge capacity retentions of $\text{LiFePO}_4/\text{Li}$ cells with different electrolytes (a) at $+60\text{ }^\circ\text{C}$ and (b) at $-20\text{ }^\circ\text{C}$. The discharge rate is 0.5 C .

3.3. Capacity Retentions of $\text{LiFePO}_4/\text{Li}$ Cells with Different Charge–Discharge Rates or at Different Temperatures. Figures 3 and 4 summarize the capacity retentions of $\text{LiFePO}_4/\text{Li}$ cells with 0.5 C of discharge rate at different temperatures. Figure 3 shows that the discharge capacities obviously increase with a rise of the temperature in both of the cells with LiODFB-SL/DMS and LiODFB-SL/DES electrolytes. We can explain this from two sides:⁹ On the one

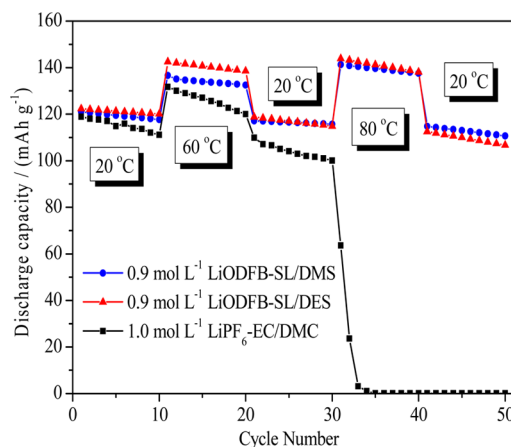


Figure 3. Cycling performances of $\text{LiFePO}_4/\text{Li}$ cells with different electrolytes at high temperatures with 0.5 C of discharge rate.

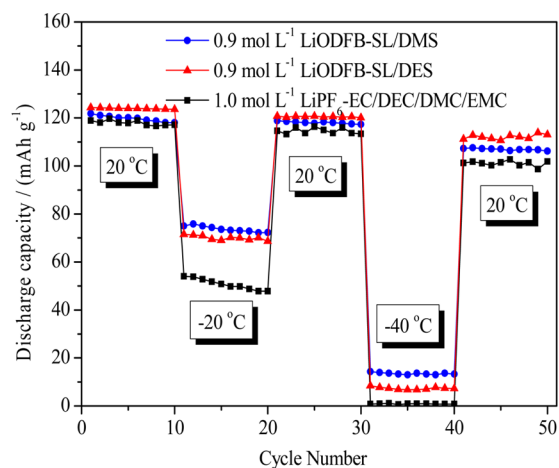


Figure 4. Cycling performances of LiFePO₄/Li cells with different electrolytes at low temperatures with 0.5 C of discharge rate.

hand, the Li⁺ ion migration velocity will increase at high temperature. On the other hand, the polarization resistance will reduce for more sufficient utilization of the active ingredients. However, traditional researches prove that when the temperature reaches 60 °C, the discharge capacity starts to decrease rapidly in the LiPF₆-based cell.⁹ This means that LiODFB-based cells are more thermally stable than the LiPF₆-EC/DMC cell at high temperature. The reason may be due to the fact that the LiPF₆-based cell is damaged by the decomposition of LiPF₆ at 60 °C. That has been further confirmed by the experimental result that only the electrochemical performance of the LiODFB-based cell could approximately recover to its original state at 20 °C after working at 60 and 80 °C for a time.

As shown in Figure 4, low-temperature capacity retentions of LiFePO₄/Li cells with LiODFB-SL/DMS, LiODFB-SL/DES, and LiPF₆-EC/DEC/DMC/EMC electrolytes were studied. With a decrease of the temperature, all of their discharge capacities dropped, and the one with the LiPF₆-EC/DEC/DMC/EMC electrolyte is more severe than the others. After working at -20 °C for 10 cycles, each of the coin cells could approximately recover to its original state at 20 °C, including the fact that the decrease of the discharge capacity is reversible in this case. However, after working at -40 °C for 10 cycles, all of the discharge-capacity restorabilities will drop, especially for the LiPF₆-EC/DEC/DMC/EMC electrolyte. That may be due to the fact that a trace of solid material will emerge from electrolytes at -40 °C, and solid precipitation is difficult to redissolve.

3.4. Electrochemical Characteristics of the First Cycles of Li/MCMB cells. The charge–discharge characteristics of Li/MCMB cells containing different electrolyte systems are further investigated and illustrated in Figures 5 (+60 °C) and 6 (-20 °C). As shown in Figure 5, although comparable lithiation capacities are obtained with the cells evaluated, it should be noticed that cells based upon LiODFB-based electrolytes take more energy to form SEI layers compared with the LiPF₆-EC/DMC electrolyte at 60 °C. The reason and its effect on a cell have been discussed in our previous research.¹² In order to effectively evaluate the property of candidate low-temperature solutions, electrolyte formulations were investigated in Li/MCMB half-cells at -20 °C. In addition to observation of reductions in the discharge and charge capacities, an obvious increase in energy consumption is observed with the LiPF₆-EC/

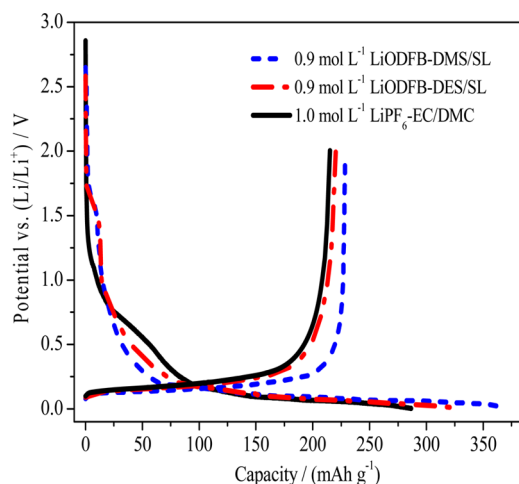


Figure 5. First discharge–charge curves of Li/MCMB cells with different electrolytes at +60 °C.

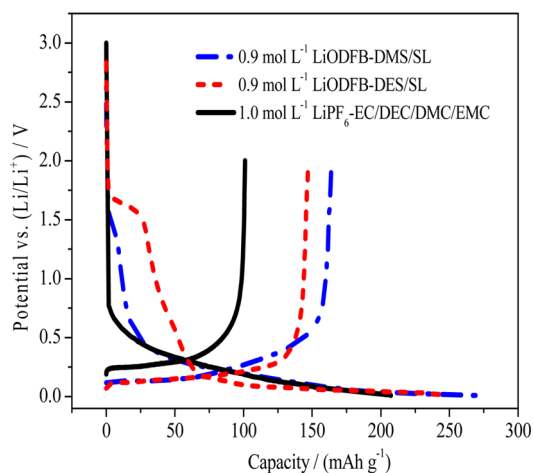


Figure 6. First discharge–charge curves of Li/MCMB cells with different electrolytes at -20 °C.

DEC/DMC/EMC electrolyte. This indicates that low-temperature conditions will thicken the resulting SEI layer during the first graphite–lithiation cycle.

3.5. Scanning Electron Microscopy (SEM) Spectra of Surfaces of Carbonaceous Anode Materials. The SEM spectra of carbonaceous anode surfaces before and after the initial lithiation process at different temperatures with different electrolytes are shown in Figure 7. Although SEI layers are formed on the anode surfaces, the structures of the SEI layers are obviously different with different formation mechanisms.¹⁶ Compared to Figure 7a, the MCMB surfaces are completely covered by dense and regular layers in parts b and d of Figure 7, benefitting from the good film-forming property of LiODFB-SL/DMS and LiODFB-SL/DES electrolytes, respectively. However, the film coverage is incomplete and irregular after a high-temperature lithiation process for the LiPF₆-EC/DMC electrolyte (Figure 7f), indicating that the SEI layer for the LiPF₆-based electrolyte is unstable and easily damaged at elevated temperature. As a result, the high-temperature cycling stability would be improved for cells with LiODFB-SL/DMS and LiODFB-SL/DES electrolytes, taking into account that a dense and regular layer could help to reduce the direct contact between the MCMB surface and the electrolyte.

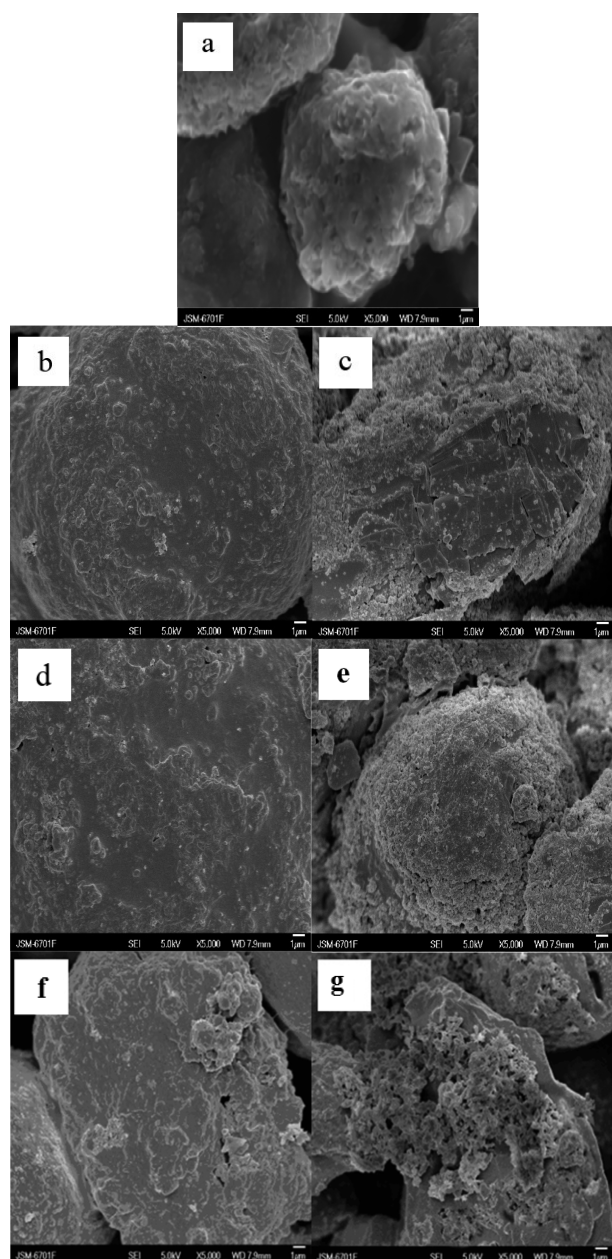


Figure 7. SEM spectra of carbonaceous anode surfaces before (a) and after the initial lithiation process at different temperatures with different electrolytes: (b) 0.9 mol L⁻¹ LiODFB-SL/DMS at 60 °C; (c) 0.9 mol L⁻¹ LiODFB-SL/DMS at -20 °C; (d) 0.9 mol L⁻¹ LiODFB-SL/DES at 60 °C; (e) 0.9 mol L⁻¹ LiODFB-SL/DES at -20 °C; (f) 1.0 mol L⁻¹ LiPF₆-EC/DMC at 60 °C; (g) 1.0 mol L⁻¹ LiPF₆-EC/DEC/DMC/EMC at -20 °C.

Although SEI layers still can be formed on MCMB surfaces at -20 °C (Figure 7c,e,g), the resulting layers are much rougher than the ones at 60 °C. These films are bad for the uniform migration of Li⁺ ions and will have far worse damage to low-temperature power performances. Because of the fact that the film resulting from the LiPF₆-EC/DEC/DMC/EMC electrolyte is more irregular than the others, the low-temperature performance of LiPF₆-based cells will not be as good as that of LiODFB-based cells.

3.6. Impedance Characteristics of Li/MCMB Cells after the Initial Cycles at Different Temperatures. ac impedance is known to be closely associated with the lithium-ion

conductivity of the SEI layer. The impedance variations of Li/MCMB cells after the initial cycles at +60 and -20 °C were investigated by EIS analysis, as shown in Figure 8. The radii of

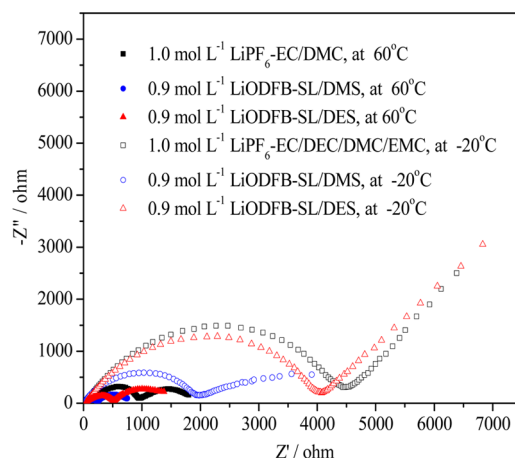


Figure 8. EIS data of Li/MCMB cells in different electrolytes after the initial cycle at different temperatures. All data are taken at a stalling state of 0.01 V.

the semicircle of cells with LiODFB-SL/DMS and LiODFB-SL/DES electrolytes are smaller than that of the cell with LiPF₆-based electrolytes after the initial cycles at +60 and -20 °C, respectively, implying that the resistance of the interface film is obviously decreased when using LiODFB-SL/DMS and LiODFB-SL/DES electrolytes.^{16,17} The reduction of SEI impedance is an important benefit for lithium-ion batteries with wide operating temperature range. Besides, it should be noticed that, at -20 °C, the cell with the LiODFB-SL/DMS electrolyte has much smaller impedance than the cell with the LiODFB-SL/DES electrolyte. A possible reason is that more LiODFB and solvents are coreduced at about 1.6 V for the LiODFB-SL/DES electrolyte.¹³

3.7. FTIR Measurements of the SEI Layers on the Surfaces of Carbonaceous Anode Materials. To investigate the possible mechanism of impedance reduction, FTIR spectra of SEI layers on anodes in Li/MCMB cells with 0.9 mol L⁻¹ LiODFB-SL/DMS and 0.9 mol L⁻¹ LiODFB-SL/DES electrolytes before and after the initial cycle at different temperatures were studied, respectively. As shown in Figure 9, both samples contain some similar transmittance peaks. The presence of lithium oxalate is supported by peaks at ~1646 and 1296 cm⁻¹. Peaks emerging at 1080.52 cm⁻¹ [$\nu_{as}(\text{SO}_3^- \text{M}^+)$] and 733.67 cm⁻¹ [$\nu_s(\text{SO}_3^- \text{M}^+)$] demonstrate the existence of Li₂SO₃. Peaks emerging at 1110.4 cm⁻¹ [$\nu(\text{SO}_4^{2-})$] and 571.65 cm⁻¹ [$\gamma(\text{SO}_4^{2-})$] demonstrate the existence of Li₂SO₄, and peaks emerging around 1108.74 cm⁻¹ [$\nu(\text{S}=\text{O})$], 2950.74 cm⁻¹ [$\nu_{as}(\text{CH})$], and 2878.68 cm⁻¹ [$\nu_s(\text{CH})$] are attributed to the existence of the sulfur-containing compound of R₁SO₂CH₂R₂ (R₁ and R₂ denote H, Li, or alkyl, respectively). The results are consistent with relevant studies.^{9,10} Because of the existence of rich sulfurous compounds, which are better conductors of Li⁺ ions than analogical carbonates, the impedances of these novel electrolytes obviously become small. Also, for peak areas of sulfurous compounds, the high-temperature samples are bigger than the low-temperature samples, indicating that high temperature is favorable for the formation of sulfurous compounds.

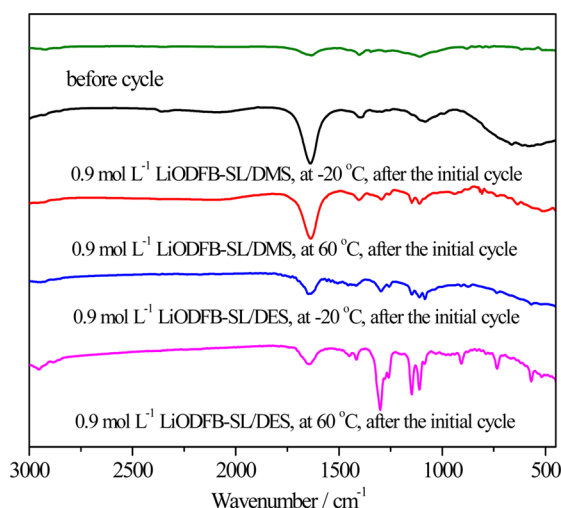


Figure 9. FTIR spectra of SEI layers on anodes in Li/MCMB cells with 0.9 mol L^{-1} LiODFB-SL/DMS and 0.9 mol L^{-1} LiODFB-SL/DES electrolytes before and after the initial cycle at different temperatures, respectively.

3.8. Cycling Performances of MCMB/Li Cells. Parts a and b of Figure 10 show the cycling performances of MCMB/Li half-cells using different electrolytes with 0.1 C of charge rate at +60 and $-20 \text{ }^{\circ}\text{C}$, respectively. As we expected, cells with both LiODFB-based electrolytes show much lower capacity fading than those with the $\text{LiPF}_6\text{-EC/DMC}$ electrolyte at high temperatures and the $\text{LiPF}_6\text{-EC/DEC/DMC/EMC}$ electrolyte at low temperatures.

4. CONCLUSIONS

Combining many advantages of LiODFB salts with those of SL/DMS and SL/DES solvents, LiODFB-SL/DMS and LiODFB-SL/DES may alternative electrolytes for wide-temperature-rang operation. From the study on the electrochemical performances of these two kinds of novel electrolytes over a wide temperature range, both LiODFB-SL/DMS and LiODFB-SL/DES electrolytes have stable cycling performance, good rate performance, and excellent film-forming characteristics. This indicates that both of those two novel electrolytes are alternative candidates for wide-temperature-range lithium-ion batteries.

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Notes

The authors declare no competing financial interest.

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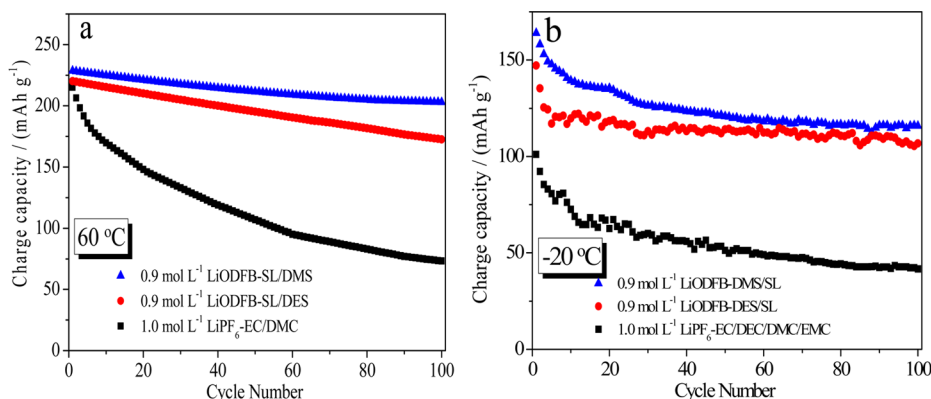


Figure 10. Charge capacity retentions of MCMB/Li cells with different electrolytes at (a) +60 and (b) $-20 \text{ }^{\circ}\text{C}$, respectively. The charge rate is 0.1 C.

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