



Short communication

Lithium difluoro(oxalato)borate/ethylene carbonate + propylene carbonate + ethyl(methyl) carbonate electrolyte for LiMn_2O_4 cathode

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ARTICLE INFO

Article history:

Received 14 May 2009

Received in revised form 23 July 2009

Accepted 14 August 2009

Available online 22 August 2009

Keywords:

Lithium-ion batteries

Lithium difluoro(oxalato)borate

Electrolyte

 LiMn_2O_4 cathode

ABSTRACT

Lithium difluoro(oxalato)borate (LiODFB) was investigated as a lithium salt for non-aqueous electrolytes for LiMn_2O_4 cathode in lithium-ion batteries. Linear sweep voltammetry (LSV) tests were used to examine the electrochemical stability and the compatibility between the electrolytes and LiMn_2O_4 cathode. Through inductively coupled plasma (ICP) analysis, we compared the amount of Mn^{2+} dissolved from the spinel cathode in 1 mol L^{-1} $\text{LiPF}_6/\text{EC} + \text{PC} + \text{EMC}$ (1:1:3 wt.%) and 1 mol L^{-1} $\text{LiODFB}/\text{EC} + \text{PC} + \text{EMC}$ (1:1:3 wt.%). AC impedance measurements and scanning electron microscopy (SEM) analysis were used to analyze the formation of the surface film on the LiMn_2O_4 cathode. These results demonstrate that ODFB anion can capture the dissolution manganese ions and form a denser and more compact surface film on the cathode surface to prevent the continued Mn^{2+} dissolution, especially at high temperature. It is found that LiODFB, instead of LiPF_6 , can improve the capacity retention significantly after 100 cycles at 25°C and 60°C , respectively. LiODFB is a very promising lithium salt for LiMn_2O_4 cathode in lithium-ion batteries.

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1. Introduction

LiMn_2O_4 with a spinel structure has attracted significant interest as a cathode material because of its high voltage, low cost, and small environmental impact. However, it has problems with capacity that it is difficult to provide a long cycle and calendar life, especially after cycling at high temperature. The erosion to LiMn_2O_4 of electrolyte is a crucial cause for capacity fading and poor cycling performance [1–7]. It was confirmed that LiBOB could work more efficiently as a lithium salt in electrolyte than LiPF_6 to inhibit the Mn^{2+} dissolution. Due to the stable film formed on the cathode surface in LiBOB-based electrolyte, the cycling performance was dramatically improved, especially at high temperature [8,9]. Nevertheless, such drawbacks lie in LiBOB as its bad solubility in linear carbonates and its high viscosity and low conductivity of LiBOB-based electrolyte.

Recently, a novel lithium salt, lithium oxalyldifluoroborate (LiODFB), has drawn intensive attention because of its significant merit [10–12]. Because its chemical structure is similar to LiBOB, a stable solid electrolyte interface (SEI) can be formed on the graphite anode, protecting it from being eroded by solvent, such as propylene carbonate (PC). Similar to anode, the cathode is also covered by a surface film after cycling in electrolytes, due to reac-

tions with solution components. The electrochemical behavior of cathode material may depend very strongly on its surface chemistry in solutions and phenomena such as surface film formation [13,14].

The previous work about LiODFB was mainly focused on characterization of the reaction on graphite anode, whereas the influences of LiODFB on cathode material, such as LiMn_2O_4 , were not reported or elaborated. In this paper, we evaluate LiODFB/EC + PC + EMC electrolyte from the standpoint of the properties that suppress Mn dissolution and film formation on the surface LiMn_2O_4 electrodes. We also report the significant improved cycling performance. The results were compared with those of LiPF_6 .

2. Experimental

2.1. Cell preparation

The electrolytes were prepared by dissolving 1 mol L^{-1} LiPF_6 or 1 mol L^{-1} LiODFB in a (1:1:3 wt%) blend of ethylene carbonate (EC), propylene carbonate (PC), and ethyl(methyl) carbonate (EMC). In order to investigate the electrochemical properties of LiMn_2O_4 cathode in different electrolytes, we assembled the 2016 type coin half-cells. LiMn_2O_4 and Li film were employed as the cathode active material and the anode active material, respectively. Celgard 2400 polyethylene/poly-propylene acted as the separator. All reagents were battery grade. The electrolytes and cells were prepared in an Ar-filled glove box.

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2.2. Measurements

Room temperature (25 °C) and high temperature (60 °C) charge–discharge tests were carried out with the utilization of LiMn₂O₄/Li half-cells. The test cells were cycled using a Land BT-10 Tester (Wuhan, China) between 2.75 V and 4.2 V at 0.5 C.

A CH Instrumental Electrochemical Workstation (CHI660A) with a three-electrode system incorporating LiMn₂O₄ and Pt as the working electrode, respectively, and Li foils as counter and reference electrodes was used for linear sweep voltammetry (LSV) at the scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed with a CH Instrumental Electrochemical Workstation (CHI660A). The data was collected at the voltage equal to 4.0 V with a frequency sweep from 0.01 Hz to 100 kHz during the measurements. The voltage in this article is relative to Li/Li⁺.

The cells were dissected after testing at 25 °C and 60 °C, respectively. Their electrodes were taken out. The electrodes were soaked in and rinsed with pure DMC to remove the residual electrolyte. Then the washed electrodes were dried in a vacuum drier. The electrodes morphologies were observed by Hitachi S-4800 SEM equipment.

An appropriate amount of LiMn₂O₄ powder was immersed in the two different electrolyte solutions, respectively. The powder/electrolyte solution was stored at 60 °C for one week. The spinel powders were filtered from the electrolytes after storage, and the manganese contents of the electrolytes were analyzed using an inductively coupled plasma (ICP) spectrometer (Thermo Fisher Scientific, 6500).

3. Results and discussion

3.1. LSVs of Pt electrode and LiMn₂O₄ electrode in different electrolytes

Fig. 1 displays LSVs of Pt electrode using 1 mol L⁻¹ LiPF₆/EC:PC:EMC (1:1:3 wt.%) and 1 mol L⁻¹ LiODFB/EC:PC:EMC (1:1:3 wt.%) as electrolytes, respectively. As we can see from Fig. 1, during the anodic potential sweeping, the oxidation reactions happened. The results indicated that the decomposition voltage of LiPF₆-based electrolyte was 4.4 V, a little lower than that (4.5 V) of LiODFB-based electrolyte, which was higher than the normal operating potential window of lithium-ion batteries. In addition, the decomposition current of LiPF₆-based electrolyte started to increase rapidly at 4.4 V, while the decomposition current of LiODFB-based electrolyte grew more slowly until the decompo-

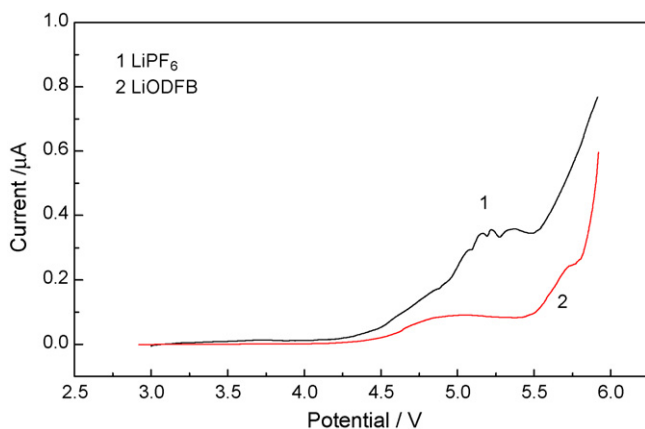


Fig. 1. LSVs of Pt electrode using 1 mol L⁻¹ LiPF₆/EC:PC:EMC = 1:1:3 and 1 mol L⁻¹ LiODFB/EC:PC:EMC = 1:1:3, scan rate 0.1 mV s⁻¹.

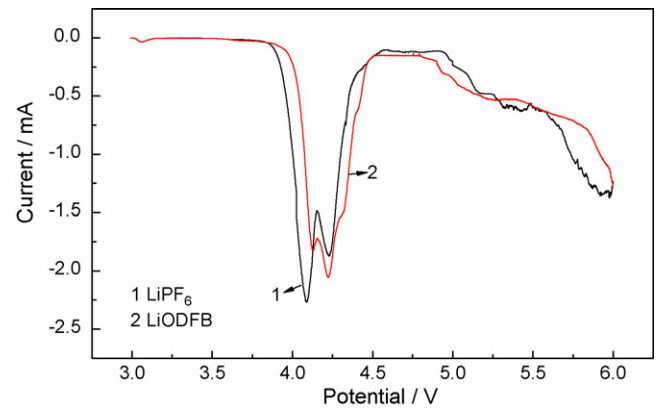


Fig. 2. LSVs of LiMn₂O₄ electrode using 1 mol L⁻¹ LiPF₆/EC:PC:EMC = 1:1:3 and 1 mol L⁻¹ LiODFB/EC:PC:EMC = 1:1:3, scan rate 0.1 mV s⁻¹.

sition voltage was higher than 5.5 V. The results suggested that the electrochemical stability of the LiODFB-based electrolyte was better than that of LiPF₆. In another words, LiODFB as a kind of lithium salt in the electrolyte was more suitable in lithium-ion batteries.

Fig. 2 shows the first LSVs of LiMn₂O₄ electrodes with the two different electrolytes. There were two obvious anodic peaks in each curve on the voltammogram, which should be associated with the two-step process of lithium-ion extraction from LiMn₂O₄ cathode [15]. The voltage of the two peaks in LiODFB-based half-cell was a little higher than that of LiPF₆-based half-cell. It was about 4.9 V when the peak appeared which was believed to be solvent oxidization on the cathode in the LiODFB-based cell, while the oxidization peak appeared at 5 V in the LiPF₆-based cell. The results suggested that LiODFB-based electrolyte did not influence the electrochemical performance of LiMn₂O₄ electrode and had good electrochemical compatibility with LiMn₂O₄ electrode in the working-voltage range.

3.2. Impedance analysis

We attempted to observe impedance changes of the cells, to understand the resistance of the interface film formed on the cathode surface. The cells were measured before and after room-temperature cycling, as well as after cycling at 60 °C. The impedance spectra of the LiMn₂O₄ half-cells containing the two different electrolytes are shown in Fig. 3. As shown in Fig. 3, the EIS of cells before cycling consisted of two parts: a semicircle at high and medium frequency and a sloping line at the low frequency. It sug-

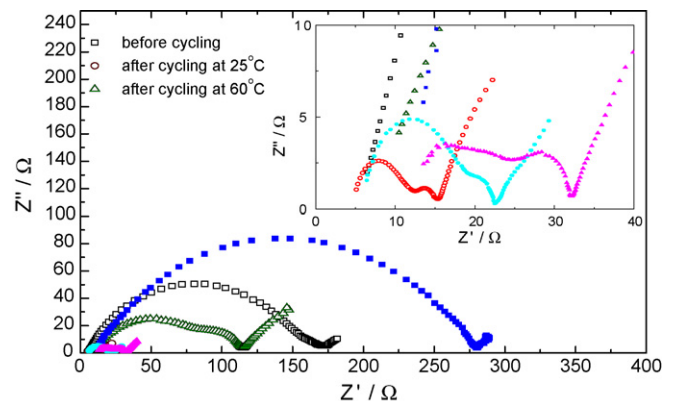


Fig. 3. EIS data for LiMn₂O₄ electrodes in the two salt solutions: 1 M LiPF₆ solution (hollow) and 1 M LiODFB solution (solid).

gested that the surface film was not formed yet, because of the absence of passive film resistance and its relative capacitance. AC of cells after cycling formed two overlapping semicircles at the high and medium frequency ranges, and a sloping line at the low frequency range. They represented the resistance (R_f) and capacitance (C_f) of the interface film, the charge-transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), and the Warburg impedance arising from the diffusion of the lithium ion in the electrode (R_T) [16,17]. The cells impedance yielded two semi-circle features after cycling, predicating the formation of the surface film. From Fig. 3, the radius of the first semi-circle of the LiODFB-based cell was a little bigger than that of LiPF₆-based cell after cycling at room temperature, which implied that the resistance of the interface film of LiODFB-based cell was higher. We could conclude that the surface film formed in LiODFB-based electrolyte was thicker than that in LiPF₆-based electrolyte [18–20].

After cycling at 60 °C, the overall impedance of LiMn₂O₄/Li cells increased visibly. The resistance of the interface film of the LiPF₆ cell was much higher than LiODFB cell. The increase of R_f was closely related to the unstable film formed on the LiMn₂O₄ surface. This indicated that the surface film in the LiODFB electrolyte was more stable than that in the LiPF₆ electrolyte and Li-ion could move more effectively in LiODFB cell at elevated temperature.

3.3. SEM analysis

Fig. 4 shows the SEM images of the LiMn₂O₄ electrodes taken from the cells with the two electrolytes, which cycled at room tem-

perature and high temperature, respectively. The surface images of LiMn₂O₄ electrodes cycled with LiPF₆-based and LiODFB-based electrolyte at 25 °C, are shown in Fig. 4a and b, respectively. In Fig. 4a, we can see that the surface of the LiMn₂O₄ electrode in LiPF₆-based electrolyte was rough and erratic, and there were large particles and gaps among them. In contrast, the surface of the LiMn₂O₄ electrode in LiODFB-based electrolyte was covered by a more intact, smoother and denser film. Therefore, LiODFB-based electrolyte could effectively form a compact film on LiMn₂O₄ electrode.

The SEM images of LiMn₂O₄ electrodes cycled at 60 °C with LiPF₆-based and LiODFB-based electrolyte are shown in Fig. 4c and d. In Fig. 4d, the covering of film on the cathode surface in LiODFB-based electrolyte was still compacted, while the covering of film on the cathode surface was more uncompacted after high-temperature cycling in LiPF₆-based electrolyte (Fig. 4c). On the surface of the electrode in LiPF₆-based cell, the covering became more irregular. This indicated that LiODFB electrolyte was not able to erode the electrode [18].

3.4. ICP analysis

In order to understand the stability of the LiMn₂O₄ material in the two electrolytes, we measured the content of Mn²⁺ in different LiMn₂O₄ powder/electrolytes, which were stored at 60 °C for one week. The amount of Mn ions dissolved from LiMn₂O₄ powder in the two different electrolytes was compared in Fig. 5. As we can see, 12.9 ppm of Mn ions was observed in LiPF₆-based electrolyte,

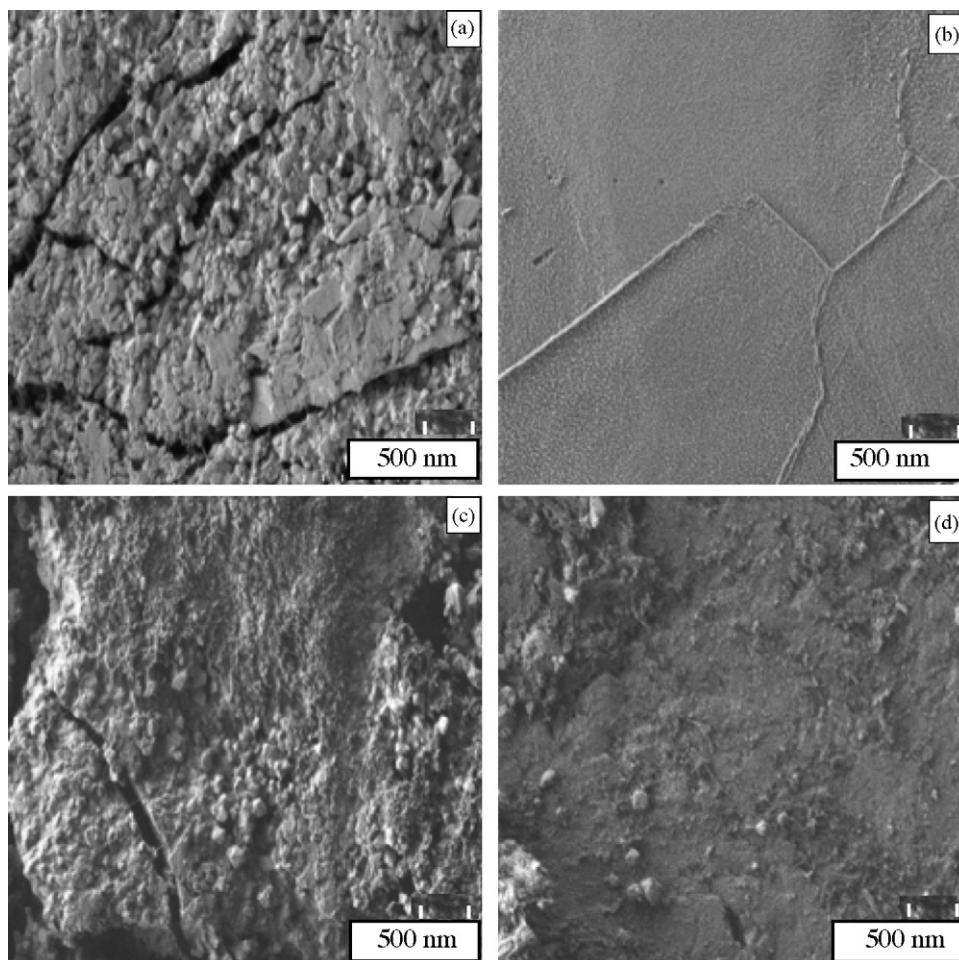


Fig. 4. SEM images of the LiMn₂O₄ electrode: (a) after cycling in LiPF₆-based electrolyte at 25 °C; (b) after cycling in LiODFB-based electrolyte at 25 °C; (c) after cycling in LiPF₆-based electrolyte at 60 °C and (d) after cycling in LiODFB-based electrolyte at 60 °C.

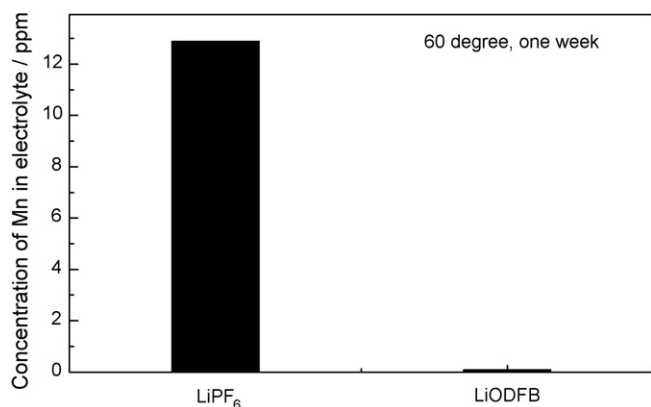


Fig. 5. Concentration of Mn^{2+} ions dissolved from LiMn_2O_4 powder stored in 1.0 M $\text{LiPF}_6/\text{EC}:\text{PC}:\text{EMC}$ (1:1:3) and 1.0 M $\text{LiODFB}/\text{EC}:\text{PC}:\text{EMC}$ (1:1:3) for one week at 60°C .

while less than 0.1 ppm of Mn ions were dissolved in the case of LiODFB-based electrolyte. The dissolution of Mn ions from spinel into the electrolyte was due to the disproportionation reaction on the surface of the spinel electrode, caused by HF attack generated by fluorine from PF_6^- and protons from electrolyte impurities, at elevated temperature [21,22]. The result illuminated that in spite of the presence of fluorine in LiODFB, it did not generate a mass of HF to erode LiMn_2O_4 electrode at high temperature, but to suppress the Mn^{2+} dissolution. Amine et al. [22] had demonstrated that there were almost no manganese ions found in the LiBOB-based electrolyte which was stored with LiMn_2O_4 powder at high temperature. It was expressed that BOB^- and Mn^{2+} combined together to form an insoluble film on the cathode surface. With the structure of LiODFB similar to that of LiBOB and the SEM results available, we can speculate that ODFB anion captured the dissolution manganese ions and forms a stable surface film to prevent the Mn^{2+} continuing dissolved. The film-forming mechanism is expressed in Fig. 6.

3.5. Cycling performance of Li/LiMn₂O₄ cell

Fig. 7 presents the impact of the two salts on cycling performance of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells at 25°C . It can be observed from Fig. 7,

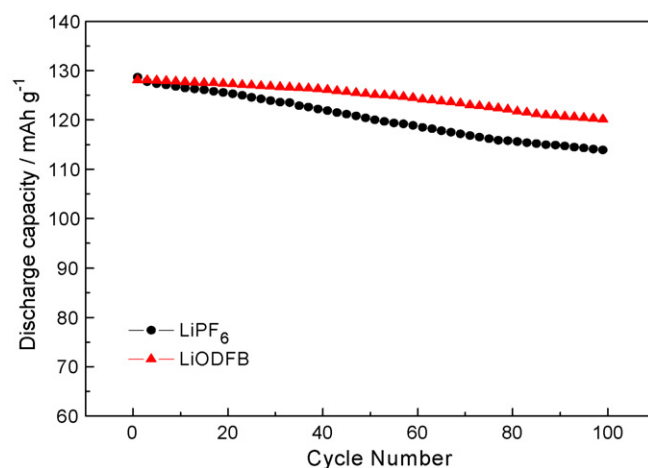


Fig. 7. Cycling performance of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells at 25°C , which was recorded at a constant rate 0.5 C and cutoff voltage from 2.75 V to 4.2 V.

the $\text{LiMn}_2\text{O}_4/\text{Li}$ cell with LiPF_6 -based electrolyte initially delivered 128.7 mAh g^{-1} and retained 113.8 mAh g^{-1} at the 100th cycle. However, when LiODFB was used as the lithium salt in the electrolyte, the $\text{LiMn}_2\text{O}_4/\text{Li}$ cell initially delivered 128.1 mAh g^{-1} and retained 120 mAh g^{-1} at the 100th cycle. At 100th cycle, the discharge capacity retention for LiODFB was 93.6%, higher than that (88.4%) of LiPF_6 . Thus, the cycling performance of the cells using LiODFB as lithium salt in electrolyte was better than the cells that using LiPF_6 as lithium salt.

Cycling performance of the $\text{LiMn}_2\text{O}_4/\text{Li}$ cells at high temperature was also evaluated. In this experiment, the cells were tested for 100 cycles at 60°C . Comparisons of different discharge capacities are summarized in Fig. 8, the discharge capacity retention was 79.2% and 87.5% for LiPF_6 and LiODFB, respectively. With the results of SEM, ICP and EIS, we can conclude that superior cycling performance, especially at elevated temperature, provided by LiODFB cells, was attributed to the more effective, compact and stable surface film formed on the LiMn_2O_4 surface. Therefore, we prefer using LiODFB as lithium salt for the preparation of the electrolyte of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells.

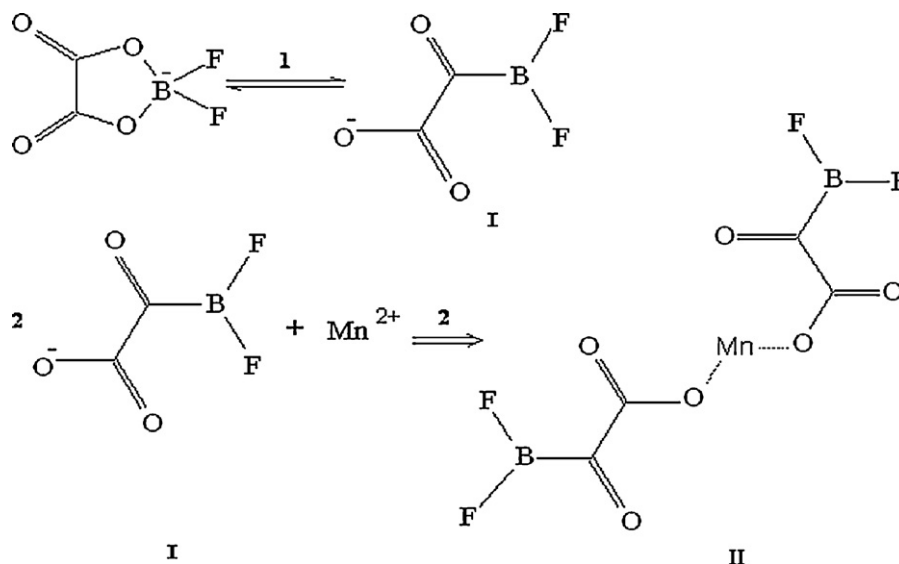


Fig. 6. Film-forming mechanism of ODFB anion acted with the dissolved Mn^{2+} .

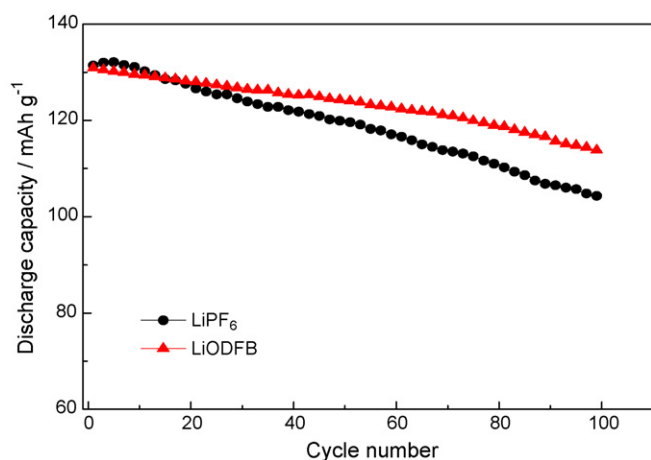


Fig. 8. Cycling performance of LiMn₂O₄/Li cells at 60 °C, which was recorded at a constant rate 0.5 C and cutoff voltage from 2.75 V to 4.2 V.

4. Conclusions

In this research, LiODFB was investigated as an alternative lithium salt to LiPF₆ in electrolyte for use with LiMn₂O₄/Li cells.

- (1) The LiODFB-based electrolyte had good electrochemical stability and compatibility with LiMn₂O₄ cathode in lithium-ion batteries.
- (2) In EIS, SEM, and ICP study, we found that the LiODFB-based electrolyte could suppress the Mn-ion dissolution. In the meantime, the surface film formed in LiODFB-based electrolyte was more effective, more compact and stable. We presumed the film-forming mechanism: the ODFB anion captured the Mn²⁺ dissolved in the electrolyte, and covered on the surface of LiMn₂O₄ cathode.

- (3) The LiODFB cells are capable of providing preferable cycling performance. At 25 °C, the capacity retention of the LiODFB cell was 93.6%, higher than the LiPF₆'s cell 88.4% capacity retention. At 60 °C, the capacity retention rises from 79.2% to 87.5% by using LiODFB instead of LiPF₆ as lithium salt.

Acknowledgment

This work was financially supported by Production and Research Project of Guangdong Province and Ministry of Education (2007A090302034).

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