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$LiPF_6$–EC–EMC electrolyte for Li-ion battery

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Abstract

We studied the effect of salt concentration and solvent ratio on the cycling performance of $LiMn_2O_4$ cathode and graphite anode in $LiPF_6$–ethylene carbonate (EC)–ethyl methyl carbonate (EMC) electrolytes. The results show that solvent ratio has negligible impact on the performance of both electrodes but does affect the issues of thermal compatibility and ionic conductivity. Salt concentration affects the performance in two reverse ways: $LiMn_2O_4$ cathode requires low concentration, while graphite anode requires high concentration. It is observed that, during the first cycle, both electrodes produce irreversible capacity and form a solid electrolyte interface (SEI) film on their surface. From the view point of operation at low temperatures, 1 M $LiPF_6$ 3:7 EC–EMC is recommended for Li-ion cells. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Li-ion battery; Electrolyte; SEI film; Spinel $LiMn_2O_4$; Graphite

1. Introduction

Li-ion battery has been widely applied to portable electronic devices, such as cameras, camcorders, and laptops, due to its relative high energy density and power [1,2]. The most popular electrolyte used in the Li-ion battery by manufacturers and researchers is $LiPF_6$ salt dissolved in a binary or ternary solvent mixture of ethylene carbonate (EC) and linear carbonates like dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). This is based on the following facts of such electrolytes: (i) $LiPF_6$ well passivates and protects Al (a material for current collector of the cathode), (ii) EC has high dielectric constant to supply high ionic conductivity, (iii) linear carbonate decreases viscosity of the electrolyte and has good penetrating ability into polyolefin-based separators, and (iv) their presence favors forming a stable solid electrolyte interface (SEI) film on the surface of graphite. It has been reported that, among the linear carbonates described above, EMC has the best thermal compatibility with EC [3]. Therefore, EC–EMC binary solvent could produce an electrolyte composition that combines low liquidus temperature and high ionic conductivity [4], which otherwise should be obtained from other ternary or quaternary solvents [5,6]. In addition, EMC was found to be more stable towards the cathode [7] and lithium metal or lithium inserted graphite compounds [8] in comparison to DMC and DEC, respectively.

The purpose of this work is to evaluate $LiPF_6$–EC–EMC electrolyte from the standpoint of electrochemical properties of spinel $LiMn_2O_4$ cathode and graphite anode, and to find an optimum composition for Li-ion battery. Because SEI films on $LiMn_2O_4$ cathode and graphite anode are formed during the initial several cycles, and the SEI films greatly affect Li-ion cell's performance [9,10], we used cyclic voltammetry or chronopotentiometry data of the first two cycles to approach an optimum electrolyte composition.

2. Experimental

Spinel $LiMn_2O_4$, supplied by FMC, was pressed onto an aluminum foil in a weight ratio of 90% $LiMn_2O_4$, 9% acetylene black, and 1% Teflon. Natural graphite (>99%, product code number LF-18A) was purchased from International Technology Exchange Society (ITE), and coated onto a copper foil using 5 wt.% of poly(vinylidene difluoride) (PVdF) as binder. Both films of $LiMn_2O_4$ and graphite electrodes were dried at 120 °C for 16 h under vacuum and then cut into 8 mm × 8 mm (0.64 cm^2) pieces, respectively. Highly pure $LiPF_6$ (>99.9%, Stella Chemica Corp.) and battery grade EC (Grant Chemical) were used as received. EMC purchased from Mitsubishi Chemical Co. was distilled

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over lithium chips before use. Electrochemical measurements were performed using an EG&G PAR Potentiostat/Galvanostat Model 273A and a three-electrode cell consisting of working electrode, lithium counter and reference electrodes. A combination of Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer, which was driven by Zplot software, was used to record electrochemical impedance spectroscopy (EIS) of the cells. The EIS was potentiostatically measured by applying a dc potential equal to open circuit voltage of the cell and an ac oscillation of 5 mV over the frequency of 100 kHz to 0.01 Hz. All operations (electrolyte preparation, cell assemble, and electrochemical tests) were conducted in an argon-filled glove box, which has both oxygen and water contents less than 20 ppm. $LiMn_2O_4$/graphite Li-ion button cell with an electrode area of 1.27 cm^2 was assembled in the glove box and galvanostatically cycled on a Maccor Series 4000 tester.

3. Results and discussion

3.1. Effect of solvent ratio

It is known that during the first cycle both $LiMn_2O_4$ cathode and graphite anode undergo a so-called formation process with the electrolyte components. This process produces irreversible capacity and forms a SEI film on their surface [7,9]. To avoid the complication caused by the initial irreversible capacity, we used the second cycle chronopotentiometry data to evaluate effect of solvent ratio on the performance of $LiMn_2O_4$ cathode. Table 1 summarizes discharge capacity and Coulombic efficiency (CE) of $LiMn_2O_4$ in 1 M $LiPF_6$ electrolytes. It is shown that the solvent ratio has negligible impact on the performance of $LiMn_2O_4$ cathode although it affects ionic conductivity and viscosity of the electrolytes [3,4]. Table 2 lists delithiation capacity and CE of graphite in 1 M $LiPF_6$ EC–EMC electrolyte for the initial three cycles. It is observed from Table 2 that there is no distinct correlation between the solvent ratio and the irreversible capacity of graphite even for the first cycle, during which a SEI film is supposed to be formed on the surface of graphite. In all three mixed solvents, graphite has around 90% of CE for the first cycle, and increases to 97% for the subsequent cycles. However, it appears that the solvent ratio influences delithiation capacity of graphite. As shown in Table 2, graphite shows the highest capacity from 1:1 EC–EMC solvent. This may relate to the interaction between ionic conductivity and viscosity of the electrolyte. That is, high EC help enhancing ionic conductivity, while more EMC favors lowering viscosity. It is known that, in the presence of carbons, EC crystallizes out of the 1:1 EC–EMC solvent at about 0 °C [11], which potentially limits the operation of Li-ion cells using it at low temperatures. Therefore, we prefer using 3:7 EC–EMC solvent for preparation of the electrolyte of Li-ion cells.

Table 1
Discharge capacity and CE of Li/$LiMn_2O_4$ cell[a]

Solvent	0.25 mA/cm^2		0.5 mA/cm^2		1.0 mA/cm^2	
	mAh/g	%	mAh/g	%	mAh/g	%
1:4 EC–EMC	119	98	116	100	110	100
1:1 EC–EMC	117	97	115	100	108	100
4:1 EC–EMC	121	97	118	100	113	100

[a] 1 M $LiPF_6$, second cycle, and solvent ratio is in wt.%.

Table 2
Charge capacity and CE of Li/graphite cell[a]

Solvent	First at 0.25 mA/cm^2		Second at 0.25 mA/cm^2		Third at 0.5 mA/cm^2	
	mAh/g	%	mAh/g	%	mAh/g	%
1:4 EC–EMC	286	90	280	97	178	98
1:1 EC–EMC	307	89	301	97	187	98
4:1 EC–EMC	268	87	256	98	154	98

[a] 1 M $LiPF_6$, and solvent ratio is in wt.%.

Fig. 1 compares the effect of the EC–EMC ratio on the electrochemical stability of electrolytes with respect to $LiMn_2O_4$ cathode. There are two pairs of very distinct current peaks between 3.9 and 4.2 V, which are known to correspond to reversible lithiation–delithiation processes of $LiMn_2O_4$ [12]. It is calculated from the cyclic voltammogram (CV) that the $LiMn_2O_4$ cathode has presents a CE of as high as 99–100%, which is independent of the EC–EMC ratio in the electrolytes. With further increase in the potential, the oxidative current has a small increase at ~5.2 V, as indicated in inset of Fig. 1. This is believed to be solvent oxidization and subsequent formation of a passive film on the cathode/electrolyte interface. The passive film is broken near 5.8 V, immediately followed by a dramatic decomposition of the solvents. Although high EC (for example, 4:1 EC–EMC solvent) helps to decrease the maximum value of decomposition current above 6 V (see Fig. 1), this benefit is not useful with dramatic decomposition taking place.

3.2. Effect of salt concentration

Performance dependence of $LiMn_2O_4$ cathode and graphite anode on the $LiPF_6$ concentration was evaluated by using 1:1 EC–EMC solvent. Table 3 compares discharge capacity and CE of $LiMn_2O_4$ cathode in EC–EMC

Table 3
Discharge capacity and coulombic efficiency of Li/$LiMn_2O_4$ cell[a]

$LiPF_6$ (M)	0.25 mA/cm^2		0.5 mA/cm^2		1.0 mA/cm^2	
	mAh/g	%	mAh/g	%	mAh/g	%
0.5	132	97	130	100	124	99
1.0	117	97	115	100	108	100
1.5	113	97	109	100	103	100

[a] In 1:1(wt.%) EC–EMC solvent, second cycle.

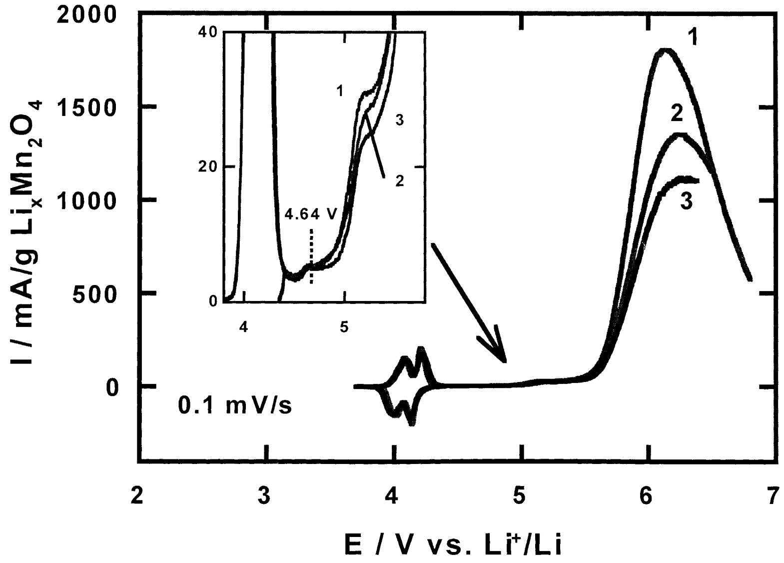

Fig. 1. Effect of solvent ratio on cyclic voltammogram of Li/LiMn$_2$O$_4$ cell in an electrolyte with 1 M LiPF$_6$ dissolved in EC–EMC mixed solvents. The CV was recorded at a scanning rate of 0.1 mV/s after the cell completed formation process.

electrolytes with different LiPF$_6$ concentration. It is seen from Table 1 that the salt concentration does not affect CE. Table 1 exhibits such a trend that discharge capacity of LiMn$_2$O$_4$ cathode increases with decreasing of LiPF$_6$ concentration. It is hard to explain this phenomenon in the terms of ionic conductivity of the electrolyte because the LiPF$_6$ concentration corresponding to the highest conductivity of 1:1 EC–EMC solvent lies around 1 M [4]. We believe that it is likely more associated with ionic conductivity of the SEI film on the surface of LiMn$_2$O$_4$ cathode. Lower LiPF$_6$ concentration may be favorable in forming the SEI film with higher ionic conductivity.

Fig. 2 plots the current response of the LiMn$_2$O$_4$ cathode to potential in 1:1 EC–EMC solutions with different LiPF$_6$ concentrations. For the similar reason described earlier, we conclude that the salt concentration hardly affects electrochemical stability of the electrolytes although 1.5 M LiPF$_6$ solution gives a lower decomposition current at ~6.0 V. It may be observed from the inset of Fig. 2 that the peak currents for reversible lithiation–delithiation processes of the LiMn$_2$O$_4$ cathode increase with an increase of LiPF$_6$ concentration in 1:1 EC–EMC solution. This result is in good agreement with the chronopotentiometry data as mentioned above.

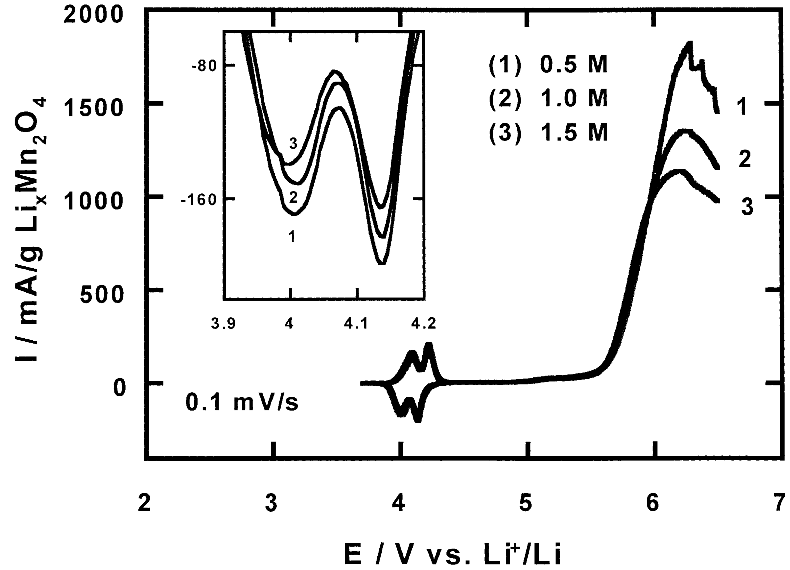

Fig. 2. Effect of LiPF$_6$ concentration on cyclic voltammogram of Li/LiMn$_2$O$_4$ cell in 1:1 EC–EMC mixed solvent. The CV was recorded at a scanning rate of 0.1 mV/s after the cell completed formation process.

Table 4
Charge capacity and coulombic efficiency of Li/graphite cell[a]

$LiPF_6$ (M)	First at 0.25 mA/cm^2		Second at 0.25 mA/cm^2		Third at 0.5 mA/cm^2	
	mAh/g	%	mAh/g	%	mAh/g	%
0.5	296	52	294	96	186	87
1.0	307	89	301	97	187	98
1.5	251	88	256	97	151	98

[a] In 1:1 (wt.%) EC–EMC solvent, second cycle.

Summarized in Table 4 are delithiation capacity and its CE of graphite in the 1:1 EC–EMC solutions having different $LiPF_6$ concentration. When the $LiPF_6$ concentration is less than 1 M, graphite produces very high irreversible capacity (CE = 52%) in the first cycle. This implies that the SEI film formed from an electrolyte with low salt concentration is not strong enough to prevent reductive decomposition of the solvents on the surface of graphite. However, higher salt concentration leads to a lower delithiation capacity (see 1.5 M in Table 4), which is probably due to the relatively low conductivity of the electrolyte and SEI film. It may be concluded from Table 4 that 1 M $LiPF_6$ is appropriate for the operation of graphite in 1:1 EC–EMC solvent.

3.3. Formation of $LiMn_2O_4$ and graphite

Based on the analyses above, we prepared 1 M $LiPF_6$ 3:7 EC–EMC electrolyte to study the formation process of the $LiMn_2O_4$ cathode and graphite anode, respectively. Fig. 3 shows CVs of the first cycle for both electrodes. For graphite anode, an irreversible reductive current appeared before major intercalation of Li-ions into graphite took place (<0.3 V). The irreversible currents are contributed to the formation of SEI film on the surface of graphite, which is always accompanied by a reductive decomposition of solvents [10,13]. For $LiMn_2O_4$ cathode, we often found met the following surprising phenomenon: open circuit voltage (OCV) of the newly assembled $Li/LiMn_2O_4$ cells is 2.7–2.9 V, and their CV of the first cycle always starts with a reductive current followed by an oxidative current peak (see Fig. 3) even we set the initial potential of 0.1 V higher than their OCV for the CV measurement. It is believed that the initial reductive current comes from lithiation of the $LiMn_2O_4$ cathode ($x\mathrm{Li}^+ + \mathrm{LiMn_2O_4} + xe \rightarrow \mathrm{Li}_{1+x}\mathrm{Mn_2O_4}$), however, the coulombs involved do not correspond to the oxidative current. By subtracting the initial electrochemical processes appearing below 3.5 V, CE of the first cycle for the $LiMn_2O_4$ cathode between 3.9 and 4.2 V is determined to be 95%. While, it falls to 75% if the whole CV in Fig. 3 is considered. This value is very close to that obtained from chronopotentiometry test. The irreversible capacity observed during the first cycle may be ascribed to the formation of SEI film. Slow scanning rate CV of the second cycle for $LiMn_2O_4$ and graphite, respectively, is plotted in Fig. 4, which indicates that both electrodes perform almost completely reversible lithiation–delithiation processes in the 1 M $LiPF_6$ 3:7 EC–EMC electrolyte. More importantly, the irreversible current has completely disappeared from both electrodes. This confirms that formation of the SEI films on the surface of electrodes takes place in the first cycle.

To understand the role of the SEI film in cell's performance, we attempt to observe impedance change of the cell before and after formation. EISs of the $Li/LiMn_2O_4$ and Li/graphite cells, respectively, are shown in Fig. 5. Typically, EIS of the newly assembled cells is mainly composed of a semicircle and a straight slope line at low frequency end (Fig. 5a and b). After the cells were cycled (formed), total impedance of the cells became small and the EIS changed into two overlapped semicircles at high and medium frequency ranges and a straight slope at low frequency end. According to previous studies [9,14,15], the semicircle at high frequencies might be explained as a parallel combination of SEI resistance and its relative capacitance, and the one at medium frequencies as a parallel combination of charge transfer resistance and double layer capacitance.

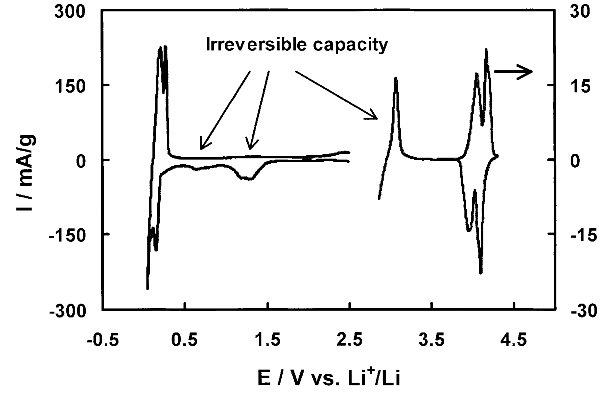

Fig. 3. Cyclic voltammograms of $LiMn_2O_4$ cathode and graphite anode in 1 M $LiPF_6$ 3:7 EC–EMC, which were recorded from the first cycle. Scan rate was 0.1 mV/s for graphite and 0.01 mV/s for $LiMn_2O_4$, respectively.

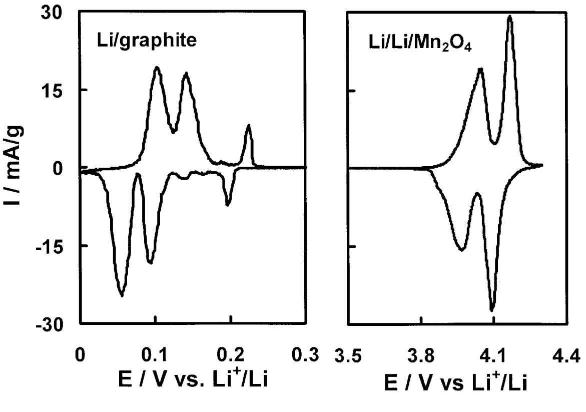

Fig. 4. Cyclic voltammograms of $LiMn_2O_4$ cathode and graphite anode in 1 M $LiPF_6$ 3:7 EC–EMC, which were recorded from the third cycle. Scan rate was 0.001 mV/s for graphite and 0.01 mV/s for $LiMn_2O_4$, respectively.

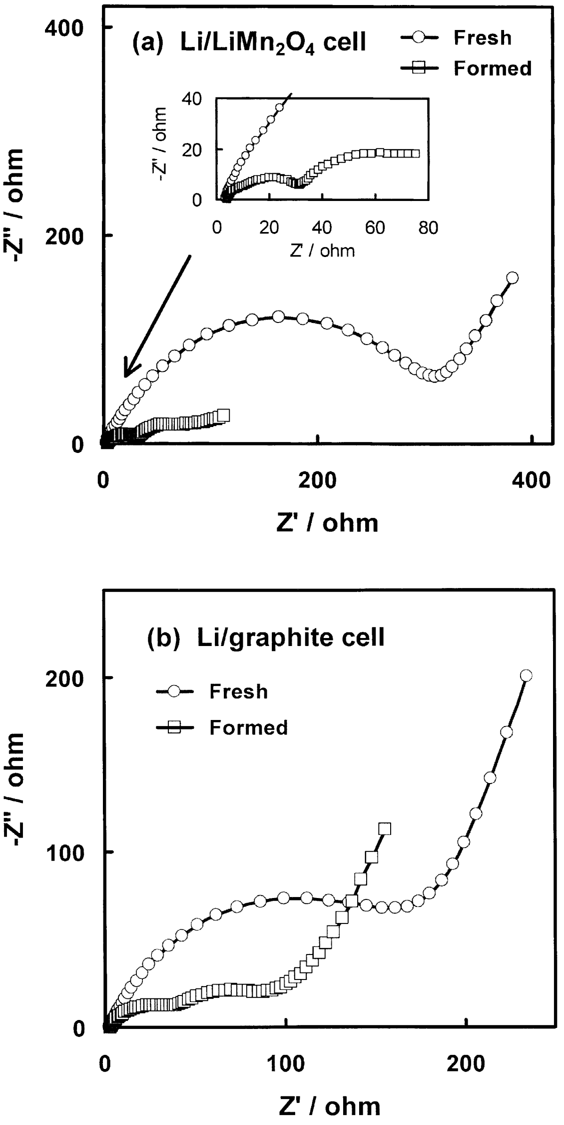

Fig. 5. Comparison of ac impedance spectroscopies for (a) Li/$LiMn_2O_4$ and (b) Li/graphite cell, respectively, before and after the formation was completed in 1 M $LiPF_6$ 3:7 EC–EMC electrolyte.

Comparing the frequency range where the semicircle appears, the only semicircle in the newly assembled cells most likely belongs to the SEI rather than charge transfer. The large diameter of the semicircles observed from the fresh cells suggests that SEI film of the newly assembled cells would be very resistive, which might be only a thin adsorbed layer [15]. After the cells were cycled, ionic conductivity of SEI film significantly improved and, therefore, the corresponding semicircle at high frequencies became much smaller.

3.4. Cycling performance of Li/$LiMn_2O_4$ cell

Fig. 6 plots charge and discharge capacity of the graphite/$LiMn_2O_4$ cell employing 1 M $LiPF_6$ 3:7 EC–EMC electrolyte as a function of cycling number. CE of the first cycle is determined to be 72%, which is close to that (75%) of Li/$LiMn_2O_4$ cell, but less that (89%) of Li/graphite. It is believed that, during the first cycle, the SEI film on the surface of $LiMn_2O_4$ cathode and graphite anode is simultaneously formed through solvent decomposition with a reverse electrochemical process. That is, some solvents are oxidized on the cathode, while the others are reduced on the graphite. Therefore, formation of the SEI film indeed consumes solvents, and the first cycle of Li-ion cells has a relatively low CE. It is observed from Fig. 6 that both charge and discharge capacity faded with an increase in the cycle number. In addition to the intrinsic defects of the $LiMn_2O_4$ cathode as reported by other researchers [15,16], solvent decomposition might be an important reason for the capacity fading. Fig. 6 shows that, starting from about 50th cycle, charge capacity becomes larger than discharge capacity (i.e. a CE of less than unity). This is a strong evidence for the solvent oxidative decomposition during charge process.

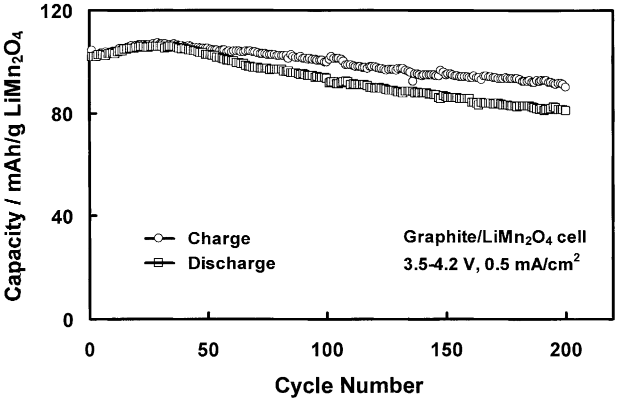

Fig. 6. Charge and discharge capacity of $LiMn_2O_4$/graphte Li-ion cell using 1 M LPF_6 3:7 EC–EMC electrolyte vs. cycle number, which was recorded at a current density of 0.5 mA/cm^2 between 3.6 and 4.2 V.

4. Conclusions

The results show that the effect of solvent ratio and salt concentration on the electrochemical stability of electrolytes with respect to the electrodes is negligible. Salt concentration plays a reverse role in affecting the performance of the $LiMn_2O_4$ cathode and the graphite anode. High salt concentration favors increasing performance of the graphite anode, but is undesirable for the $LiMn_2O_4$ cathode. Considering this reverse effect, we think that a suitable electrolyte for Li-ion cells is 1 M $LiPF_6$ 3:7 EC–EMC, which allows the cells to perform at low temperatures without EC crystallization out of the electrolyte. In the same electrolyte, both the $LiMn_2O_4$ cathode and the graphite anode were found to produce more than 10% of irreversible capacity during the first cycle, which is believed to relate to the formation of a SEI film on their surface. EIS of the Li-half cells indicates that, at room temperature, the resistance of the SEI film is comparable to the charge transfer resistance.

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