

Electrolyte for high voltage Li/LiMn_{1.9}Co_{0.1}O₄ cells

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Abstract

An electrolyte for high voltage lithium metal anode cells must simultaneously satisfy at least the following requirements: (i) high cycling efficiency on the lithium metal anode; (ii) higher oxidation potential than the charging voltage, and (iii) high specific conductivity. We have examined various electrolytes for lithium metal anode cells using a high voltage cathode, LiMn_{1.9}Co_{0.1}O₄. Of the electrolytes resistant to high voltage that we used, a system containing 60 to 90 vol.% of dimethyl carbonate (DMC) mixed with ethylene carbonate (EC) and 1.0 M lithium hexafluorophosphate (LiPF₆) provided the best cycling efficiency on a lithium metal anode, as well as a high specific conductivity around 10 mS cm⁻¹ at 20 °C. © 1997 Elsevier Science S.A.

Keywords Electrolytes, Lithium anodes; Cycling efficiency; Lithium cells

1. Introduction

Lithium metal used as the anode for a rechargeable lithium cell provides low electrochemical potential which can provide a high voltage cell, and a high energy density of 3860 mAh/g. A battery system comprising a lithium metal anode and a cathode such as LiCoO₂, LiNiO₂ or LiMn₂O₄ exhibits high performance in terms of cell voltage and energy density. However, the cycling efficiency on the lithium metal anode is less than 100% because the lithium metal reacts chemically with the solvent or solute in the electrolyte and electrochemically during charging when the lithium cations turn into lithium metal [1]. Therefore, the cycling efficiency of these cells depends on the electrolyte.

In the late 1980s, a series of rechargeable Li/LiCoO₂ cells was studied with regard to electrolytes and cell performance [2,3]. In 1990, Sony Energytec first succeeded in manufacturing a 4 V class rechargeable carbon/LiCoO₂ battery using propylene carbonate (PC), diethyl carbonate (DEC) and LiPF₆ [4]. Subsequently, several battery makers manufactured lithium-ion batteries. Moreover, various electrolyte systems were examined and applied to actual batteries [5–10]. However, these electrolytes do not always produce high levels of performance with lithium metal batteries.

We have described a dimethyl carbonate (DMC)-based electrolyte which provides good cycle performance with an

Li/LiMn_{1.9}Co_{0.1}O₄ cell [11]. This cathode has a high cycleability which is achieved by substituting part of the manganese for cobalt [12]. And the high cycleability of this cathode makes it possible to estimate the cycling efficiency on a lithium metal anode. This is because the cycle life of the Li/LiMn_{1.9}Co_{0.1}O₄ cells was determined by lithium cycling efficiency, as long as the electrolyte is resistant to oxidation up to at least the charging voltage. In this paper, we investigate cell performance and electrolyte characteristics which are dependent on the electrolyte composition.

2. Experimental

The electrolyte consisted of LiPF₆ dissolved in various compositions of mixed solvents. We used DMC, PC, ethylene carbonate (EC), DEC and ethylmethyl carbonate (EMC) as the electrolyte solvent. All the electrolytes we used contained less than 20 ppm of water. The specific conductivity of each electrolyte was measured at 1 kHz with an LCR bridge.

LiMn_{1.9}Co_{0.1}O₄ was synthesized as described previously [12]. Li/LiMn_{1.9}Co_{0.1}O₄ cells were fabricated as coin cells (23 mm in diameter, 2 mm thick). The cathode was coated on a stainless-steel or an aluminum substrate and the electrode area was 2 cm². The anode, separator and cathode were pressurized using stainless-steel spacers in the cell. The cells were charged up to 4.3 V at 1 mA/cm² and discharged down to 3.3 V at 3 mA/cm² at 20 °C. The cycle performance of the Li/LiMn_{1.9}Co_{0.1}O₄ cells was evaluated by using the figure-

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of-merit (FOM) for lithium cycling efficiency [13]. The FOM was calculated using Eq. (1). The end of the cycle is the time when the capacity has fallen to 50% of its initial value.

$$\text{FOM} = \frac{\text{accumulated discharge capacity to the end of cycle (mAh)}}{\text{theoretical lithium (anode + cathode) (mAh)}} \quad (1)$$

3. Results and discussion

1.0 M LiPF₆-PC/DMC ($x:100-x$) indicates that the solute is LiPF₆ with a concentration of 1.0 mol/l (M), and the volume ratio of PC to DMC is $x:(100-x)$, (x : vol.% of PC in a solvent mixture).

First, we studied a 1.0 M LiPF₆-PC/DMC ($x:100-x$) series. The relationship between specific conductivities and the vol.% of PC in a solvent mixture at 20 and 60 °C is shown in Fig. 1. The highest specific conductivities were obtained at $x=40$ (60 °C) and $x=30$ (20 °C) in the 0–50 vol.% PC range. Fig. 2 shows cycle performance of Li/LiMn_{1.9}Co_{0.1}O₄ cells using a series of PC/DMC electrolytes. The longest cycle life of 885 was obtained with 20 vol.% PC electrolyte. These cycling results can be transformed to FOM in order to normalize the actual cell capacity and the theoretical capacity

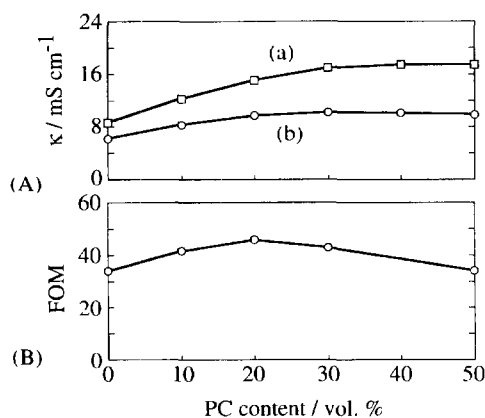


Fig. 1. (A) Specific conductivity (κ) of 1.0 M LiPF₆-PC/DMC (a) 60 °C, and (b) 20 °C. (B) FOM of Li/LiMn_{1.9}Co_{0.1}O₄ cells using 1.0 M LiPF₆-PC/DMC

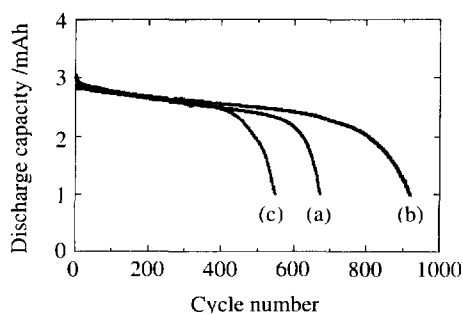


Fig. 2. Cycle performance of Li/LiMn_{1.9}Co_{0.1}O₄ cells using 1.0 M LiPF₆-PC/DMC ($x:100-x$) (a) $x=0$, (b) $x=20$, and (c) $x=50$

of an electrode in a cell. The relationship between FOM and the vol.% PC in a solvent mixture is also shown in Fig. 1. This trend of FOM with a change in PC content is similar to that of the specific conductivity at 20 °C. Therefore, it is thought that high specific conductivity provides high FOM under this cycle condition. It has been reported that cycling efficiency depends on the specific conductivity as far as the same component in a electrolyte system is concerned [14].

Next, we examined a 1.0 M LiPF₆-EC/DMC ($x:100-x$) series. The relationship between specific conductivities and the vol.% EC in a solvent mixture at 20 and 60 °C is shown in Fig. 3. The highest specific conductivities were obtained at $x=40$ (60 °C) and $x=30$ (20 °C) in the 0–50 vol.% EC range. This is the same trend as that of the PC/DMC electrolyte. The specific conductivity of EC/DMC is higher than that of PC/DMC due to the higher degree of ionic dissociation of LiPF₆ resulting from the higher dielectric constant of EC. Fig. 4 shows the cycle performance of Li/LiMn_{1.9}Co_{0.1}O₄ cells using a 1.0 M LiPF₆-EC/DMC ($x:100-x$) series. The longest cycle life of some 1300 cycles was obtained with 10–20 vol.% EC electrolyte. The relationship between FOM and the vol.% EC is also shown in Fig. 3. The electrolyte containing 10–30 vol.% EC provided a high FOM of around 60 which is equal to a 98.3% cycling efficiency on a lithium anode. This EC content range exhibits high specific conduc-

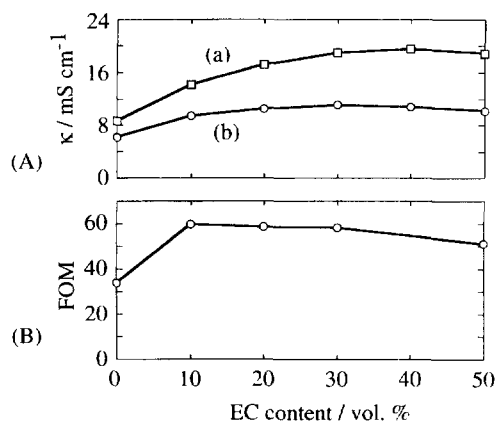


Fig. 3. (A) Specific conductivity of 1.0 M LiPF₆-EC/DMC: (a) 60 °C, and (b) 20 °C (B) FOM of Li/LiMn_{1.9}Co_{0.1}O₄ cells using 1.0 M LiPF₆-EC/DMC.

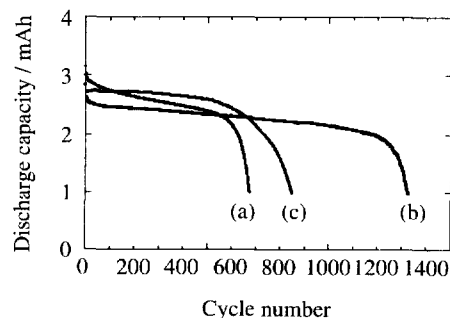


Fig. 4. Cycle performance of Li/LiMn_{1.9}Co_{0.1}O₄ cells using 1.0 M LiPF₆-EC/DMC ($x:100-x$). (a) $x=0$, (b) $x=20$, and (c) $x=50$.

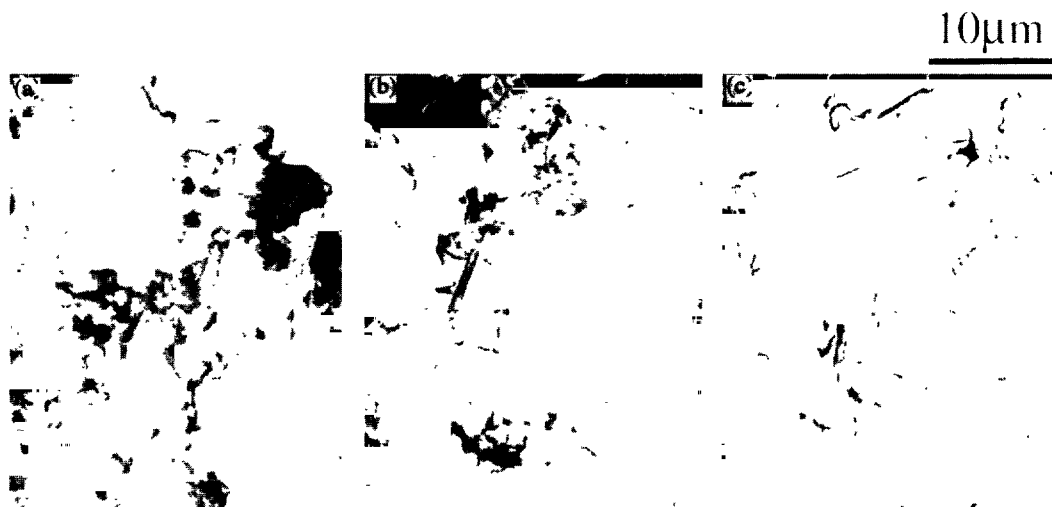


Fig. 5. SEM images of deposited lithium after 10th charge: (a) 1.0 M LiPF₆-DMC; (b) 1.0 M LiPF₆-EC/DMC (20:80), and (c) 1.0 M LiPF₆-EC/DMC (50:50)

tivity. Therefore, a high specific conductivity can provide a high FOM, as with the PC/DMC electrolyte system. Fig. 5 shows scanning electron microscopy (SEM) images of the lithium anode after the 10th charge for the three EC-mixed electrolytes. Although the morphology of the deposited lithium is fluffy for both $x=0$ and $x=50$, $x=20$ provides compact and flat lithium. We believe that these high FOMs caused by the compact and flat lithium morphology is the result of the high specific conductivity, or more exactly the high mobility of the lithium cations.

We examined a 1.5 M LiPF₆-EC/DMC ($x:100-x$) series and found that the trend was similar to that of the 1.0 M LiPF₆ electrolyte systems. However, the performance was poorer than that of the 1.0 M LiPF₆ system.

We also studied other acyclic carbonates mixed with EC. The specific conductivities of both 1.0 M LiPF₆-EC/EMC ($x:100-x$) and 1.0 M LiPF₆-EC/DEC ($x:100-x$) with x values of 0, 20 and 50 compared with EC/DMC system, are shown in Fig. 6. Neither electrolyte system exhibited maxi-

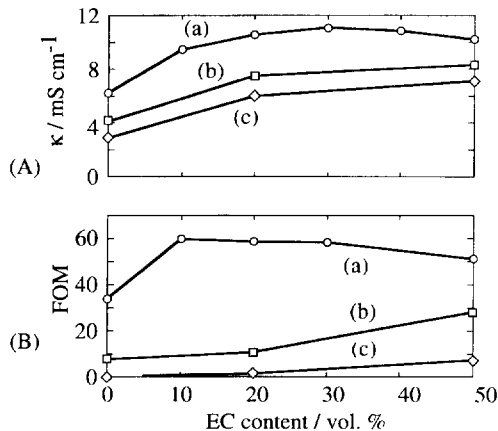


Fig. 6. (A) Specific conductivity of each EC-mixed electrolyte at 20°C. (B) FOM of Li/LiMn_{1-x}Co_{0.1}O₄ cells: (a) 1.0 M LiPF₆-EC/DMC; (b) 1.0 M LiPF₆-EC/EMC, and (c) 1.0 M LiPF₆-EC/DEC

imum specific conductivity in the range of x from 0 to 50. This is different from the EC/DMC electrolyte system. Figs. 7 and 8 show the cycle performance of Li/LiMn_{1-x}Co_{0.1}O₄ cells using 1.0 M LiPF₆-EC/EMC ($x:100-x$) and 1.0 M LiPF₆-EC/DEC ($x:100-x$), respectively. 1.0 M LiPF₆-DEC could not provide cell cycling because this electrolyte consumed the lithium metal anode. This reaction is thought to be based on the ethyl group [15]. However, DEC mixed with EC electrolyte results in some cycling because a protective film formed by EC prevents any reaction between DEC

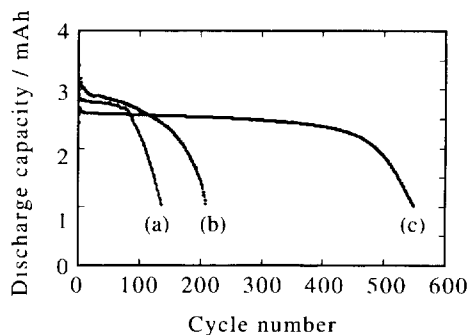


Fig. 7. Cycle performance of Li/LiMn_{1-x}Co_{0.1}O₄ cells using 1.0 M LiPF₆-EC/EMC ($x:100-x$): (a) $x=0$, (b) $x=20$, and (c) $x=50$.

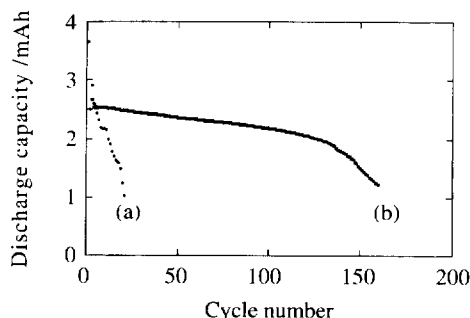


Fig. 8. Cycle performance of Li/LiMn_{1-x}Co_{0.1}O₄ cells using 1.0 M LiPF₆-EC/DEC ($x:100-x$): (a) $x=20$, and (b) $x=50$

and lithium metal [16]. EMC also reacts with lithium metal, but its reactivity is poorer than that of DEC. As a consequence, neither EMC nor DEC-mixed electrolytes could provide a better cycle performance than DMC-mixed electrolyte. The differences in reactivity and specific conductivity of each acyclic carbonate mixed with EC electrolyte, provided widely varying cycle performance results.

4. Conclusions

We examined various electrolyte compositions using cyclic and acyclic carbonate for a high voltage lithium metal cell. DMC-mixed electrolyte provides high cycleability with a lithium metal anode which is very different from the other acyclic carbonates such as EMC and DEC. For solvents mixed with DMC, EC exhibits better cycleability and specific conductivity than PC. Under our cycle conditions of high rate discharge and quick charge, the trend of FOM dependence on the electrolyte composition is similar to that of the electrolyte conductivity.

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