

Short communication

Gamma-crotonlatone as an electrolyte additive for improving the cyclability of MCMB electrode

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Abstract

In this paper, gamma-crotonlatone (GCL) was tested as an additive to electrolyte solutions of 1 M LiPF₆ EC:DMC (1:1, vol) for lithium-ion batteries. Smaller volume amount in the order of 10⁻⁶ GCL improved the cyclability of MCMB electrode, and decreased the impedance of MCMB/Li cell. The results of cyclic voltammetry show that the GCL has higher reduction decomposition potential at about 2.1 V. The surface morphologies and chemistry of the solid electrolyte interphase (SEI) film formed on MCMB electrodes cycled in 1 M LiPF₆ EC:DMC with and without GCL were studied by SEM, FTIR and XPS analyses, and the results show that a uniform, stable and low-resistive SEI film was formed on the surface of MCMB electrode, which cause the excellent cyclability of electrode.

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1. Introduction

Electrolyte based on non-aqueous organic solvent mixture of ethylene carbonate (EC) with dimethyl carbonate (DMC), and/or diethyl carbonate (DEC) is commonly used in commercial lithium-ion battery. EC is an indispensable component because of its higher dielectric constant and excellent film-forming ability, but it owns higher melting point and viscosity, which usually cause the poor low temperature performance of lithium-ion battery [1–3]. DEC or DMC is often used to decrease the viscosity of electrolyte system because of their lower viscosity. These components are electrochemically unstable on the surface of anodes, and the reduction decomposition occurs during the first cycle, which leading to a SEI film formation [4]. The presence of a protective SEI film prevents some irreversible reactions of electrolytes on anode, and also has a great influence on the safety, self-discharge, power capability, cycle life, faradic efficiency, especially the irreversible capacity loss for the first cycle in lithium-ion batteries [5–9]. So a good electrolyte system must have a better film-forming performance, in

addition to a good ionic conductivity, high chemical and electrochemical stability. However, accumulative SEI film growth result from side reactions during cycles increases both the SEI film impedance and electrochemical reaction resistance, which result in capacity fade on cycling [10–12]. On the other hand, the components of the SEI film are soluble in DMC solvent [13–14]. This corrosion of the SEI film by linear carbonate solvents would undoubtedly produce negative effects on the performance of lithium-ion batteries. During long-term cycling, the damaged SEI film has to be repaired constantly by the electrochemical and chemical reactions of organic solvents and lithium salts with the lithium ion, which consumes continuously the limited lithium-ion source in the battery, and cause capacity fading and increase the impedance at the electrode/electrolyte interphase.

Controlling the physicochemical properties of electrode surface (Li metal, lithiated carbons, and lithiated transition metal oxides) was tested an effective technique to obtain the desirable cyclic performance of electrode [15–19]. In which, the addition of electrolyte additive has been a commonly used method. For example, the pretreatment of Li metal interface with an electrolyte containing appropriate amount of AlI₃ was found to increase Li cyclability [17], and the presence of VC decreases the irreversible capacity and improves the cyclability of graphite electrode at elevated temperature [18], and biphenyl

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may improve the cycle performance of cathode materials like LiCoO_2 and LiMn_2O_4 [19].

In this paper, we introduce gamma-crotonlatone (GCL) as an additive in the EC-based electrolyte solution and explore the effect of GCL on the electrochemical behavior of MCMB electrode.

2. Experimental

Mesocarbon microbeads (MCMB) was used as a working electrode material, and metallic lithium as a counter electrode. MCMB-based electrodes were made as follows: 85% MCMB, 5% carbon black were mixed with 10% PVdF (polyvinylidene fluoride) in an organic solvent (*N*-methyl pyrrolidione, NMP), and the mixture was coated onto the copper foil substrate, then heated at 120 °C in vacuum condition. The separator was made of Celgard PP (polypropylene) membrane.

The preparations of liquid electrolytes, together with coin type cell (CR2025) assembly, were all conducted in an argon-filled glove box (*M. BRAUN*, Germany, $\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 1$ ppm). LiPF_6 (99.8% purity) and EC, DMC (99.9% purity) were purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd. (China), GCL (98% purity) was purchased from Aldrich. All the reagents were used as received without further purification. Electrolyte solutions were prepared by dissolving 1 M LiPF_6 in the mixtures of EC:DMC (1:1, vol), then add GCL into it with three different volume concentration (10^{-2} , 10^{-4} , 10^{-6}) through dilution. The electrolyte system of 1 M LiPF_6 EC:DMC (1:1, vol) was used for comparison.

The constant current charge/discharge measurements were carried out with Land Cell test. The cyclic voltammetry and electrochemical impedance spectra were used in order to understand the influence of added GCL on the electrochemical property. Both of them are performed on a CHI 660B electrochemical workstation.

After the charge–discharge test, the MCMB electrodes were separated from the coin type cell in an Argon-filled glove box and rinsed with ethanol solvent to remove electrolyte, then dried in glove box naturally. The morphologies of the SEI film were observed using scanning electron micrograph (SEM, JECO JSM-6360LV). The organic components of the SEI film were characterized by an FTIR spectrometer (EQUINOX 55). XPS (VG Microlab MK II) was used to obtain information about the elementary chemical state for the SEI film on the MCMB electrode. Both of the samples of FTIR and XPS were prepared in a manner similar to that used for the scanning electron micrographs.

3. Results and discussion

3.1. The theory foundation of additive

As is well known, electrochemistry stability, which is assessed by stable voltage window, is very important to electrolyte solvents for Li-ion batteries. In our study, we use frontier orbitals to characterize the electrochemistry stability, which can

Table 1

The frontier orbital energy for common used solvents and GCL

Solvents	LUMO energy (eV)	HOMO energy (eV)
Ethylene carbonate (EC)	1.175	−11.777
Dimethyl carbonate (DMC)	1.248	−11.623
Diethyl carbonate (DEC)	1.288	−11.450
Propylene carbonate (PC)	1.255	−11.690
Gamma-crotonlatone (GCL)	−0.464	−10.815

represent the electrochemical activity of the material. The frontier orbitals are the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and orbitals close to the two previously mentioned orbital. When electrons are added or removed from the molecule, they will be firstly added to the LUMO or removed from the HOMO. Because of it, there should be a connection between the HOMO energy and the first oxidation potential of a molecule, also the LUMO energy and the first reduction potential. As an ideal film-forming additive, which should have the property of higher reduction potential, i.e. it must be of lower LUMO energy. The data of frontier orbitals for commonly used solvents calculated by standard procedure are given in Table 1. All the calculations were performed on SGI workstation with Cerius2 software.

As seen from Table 1, the LUMO energy of GCL is lower than the commonly used solvents (EC, PC, DMC, and DEC), which implies that GCL should easily be reduced and may promote SEI formation when it is added in the mixture solvent of EC-based and PC-based. In this paper, the effect of GCL additive on the MCMB electrode was examined and the results show that GCL is a novel and effective electrolyte additive in the EC-based electrolyte.

3.2. Charge–discharge cycle

The concentration of additive plays an important role on the electrochemical performance of batteries. In general, the concentration of additive was in the order of 10^{-2} . But in our test,

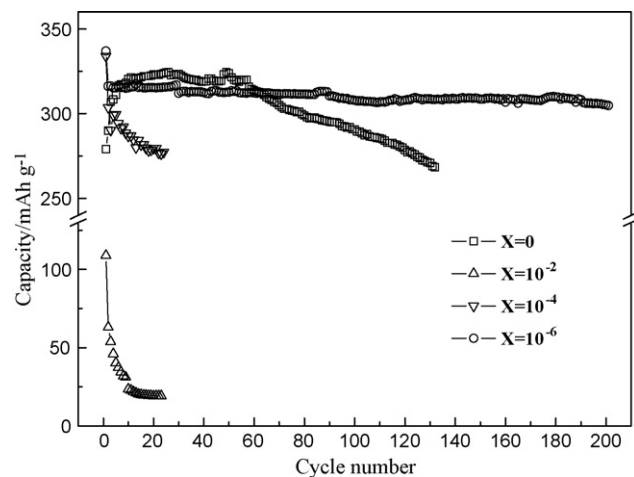


Fig. 1. The cyclability of MCMB/Li cells at room temperature in 1 M LiPF_6 EC:DMC (1:1, vol) with and without GCL (1/8C rate, 0–1.5 V). The value of X means the volume concentration of GCL in electrolyte.

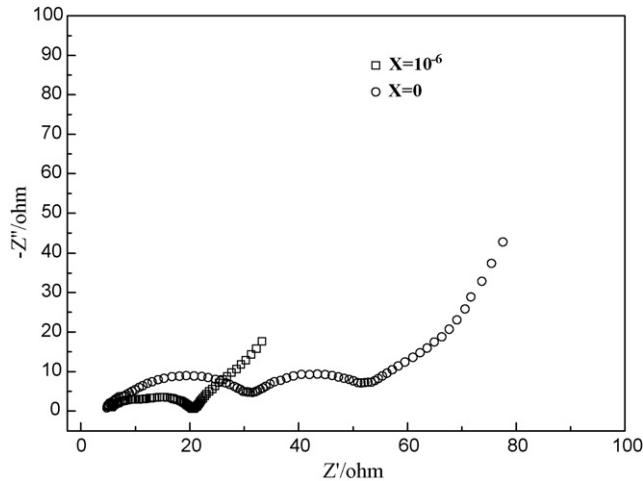


Fig. 2. Impedance spectra of MCMB/Li cells in 1 M LiPF₆ EC:DMC (1:1, vol) with and without GCL (after the first cycle; frequency range: 0.01 to 10⁵ Hz; amplitude: 5 mV).

we found that the concentration in the order 10⁻² and 10⁻⁴ all had an adverse effect on the MCMB/Li cell, until the concentration was decreased to 10⁻⁶, a favorable effect was obtained, as seen from Fig. 1. The cyclic performance of MCMB electrode has been remarkably improved by the addition of 10⁻⁶ GCL. The first and second discharge specific capacities of MCMB electrode with electrolyte containing 10⁻⁶ GCL are 336.9 and 316.2 mAh g⁻¹, and after 100 cycles, the discharge specific capacity is 307.8 mAh g⁻¹, and the capacity of the 200th cycle is 305.1 mAh g⁻¹. However, to the electrolyte without GCL, the first discharge specific capacity is 279.0 mAh g⁻¹, then during the followed cycles, the discharge specific capacity is increased and at the 10th cycle, the capacity has arrived at a steady value about 320 mAh g⁻¹, however, the capacity begins decrease from about the 60th cycle.

In comparison with the electrolyte with 10⁻⁶ GCL, it takes about 10 cycles to form a stable SEI film for electrolyte without GCL and this formation process consumes largely electrolyte and lithium ion, and causes the lower specific capacity and poor cyclability, however, we use metallic lithium as counter electrode and the lithium source is infinite, the stable specific capacity is higher than the electrolyte with 10⁻⁶ GCL. Accord-

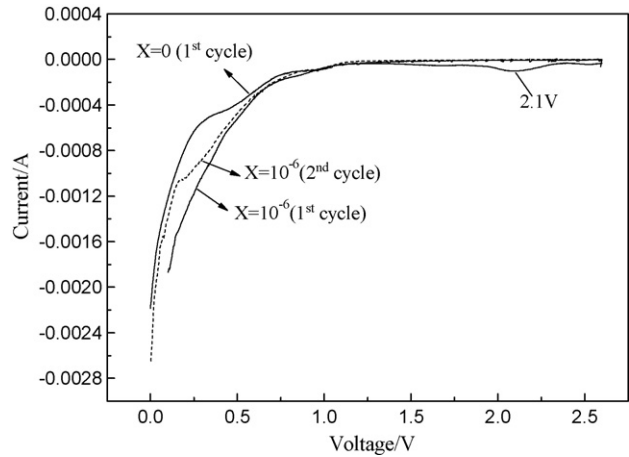


Fig. 3. The cyclic voltammetry curves of MCMB/Li cells in 1 M LiPF₆ EC:DMC (1:1, vol) with and without GCL (scan rate is 0.05 mV s⁻¹).

ing to the mechanism of the formation of SEI film [20], we speculate that the addition of a smaller concentration of GCL maybe can facilitate the growth of nuclei on the surface of the MCMB electrode, and the presence of appropriate nuclei is of great benefit to forming a uniform SEI film. But, in fact, it is difficult to explain why the addition of 10⁻⁶ GCL shows much better effect than the 10⁻².

3.3. EIS and CV measurement

Fig. 2 shows the EIS results of MCMB/Li cells cycled in electrolyte with and without GCL, which obtained at fully charged state. According to Ref. [21], we identify that the high frequency semicircle relates to Li-ion migration through the SEI film (R_f), the intermediate frequency semicircle relates to charge transfer (R_{ct}), and the low frequency behavior that appears as a ‘Warburg’ type element reflects the solid-state diffusion of Li⁺ in the MCMB electrode. The pronounced impact of the presence of GCL on the impedance behavior was found. In comparisons with the electrolyte without GCL, the decreases in the radii of the high and intermediate frequency semicircles are seen in electrolyte with GCL, which is favorable for lithium-ion transport in the SEI film and the occurrence of electrochemical reaction.

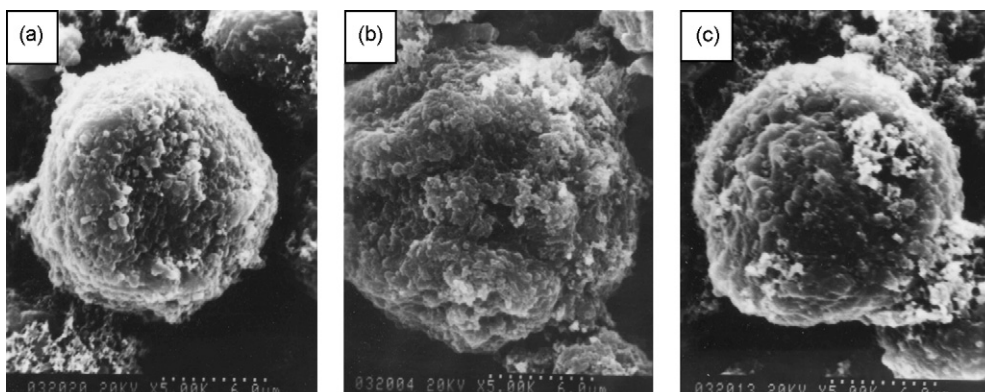


Fig. 4. The SEM spectra of MCMB electrodes cycled in different EC-based electrolytes: (a) before charge–discharge; (b) X=0; (c) X=10⁻⁶.

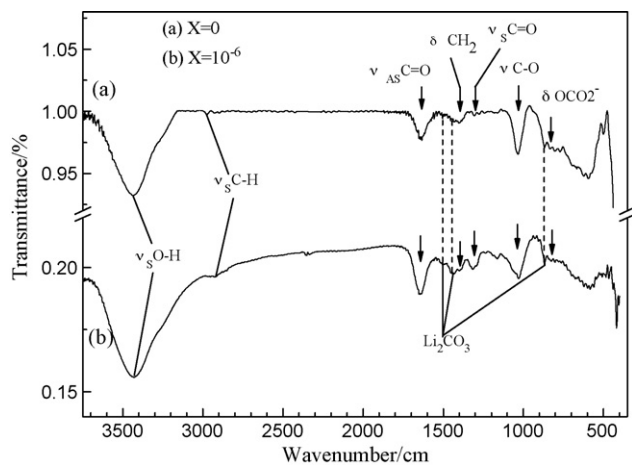


Fig. 5. The FTIR spectra of MCMB electrodes cycled in different EC-based electrolytes: (a) $X=0$ and (b) $X=10^{-6}$.

Generally, R_{ct} should not be influenced by electrolytes, however, experiences show that it is in fact easily affected by the chemical composition of the electrolytes [22]. Therefore, it should involve an interfacial process that is sensitive to the surface film formation [23].

In order to better understand the role played by GCL in EC-based electrolyte, cycle voltammetry was performed on the electrolytes with and without GCL. Fig. 3 shows CV curves for the first and the second cycle obtained from the electrolyte with GCL and CV curve for the first cycle from the electrolyte without GCL. To the electrolyte with GCL, at the first negative scan process, a reductive peak at 2.1 V was found, and this peak disappeared at the second negative scan curve. We attribute this reductive peak to the decomposition of GCL, because at the first negative scan curve of electrolyte without GCL, there is no reductive peak at this potential.

As known, the total impedance of the battery affects the cycle performance, i.e. higher impedance often causes larger polarization, smaller capacity and poor cyclability, so, the preferential reductive decomposition of GCL, which accelerate a less resistance SEI film formation, maybe the origin of the excellent cyclic performance of MCMB electrode with the electrolyte containing 10^{-6} GCL.

3.4. SEI film analyses

To further understand the effect of GCL, we test the physicochemical properties of SEI film on the surface of MCMB

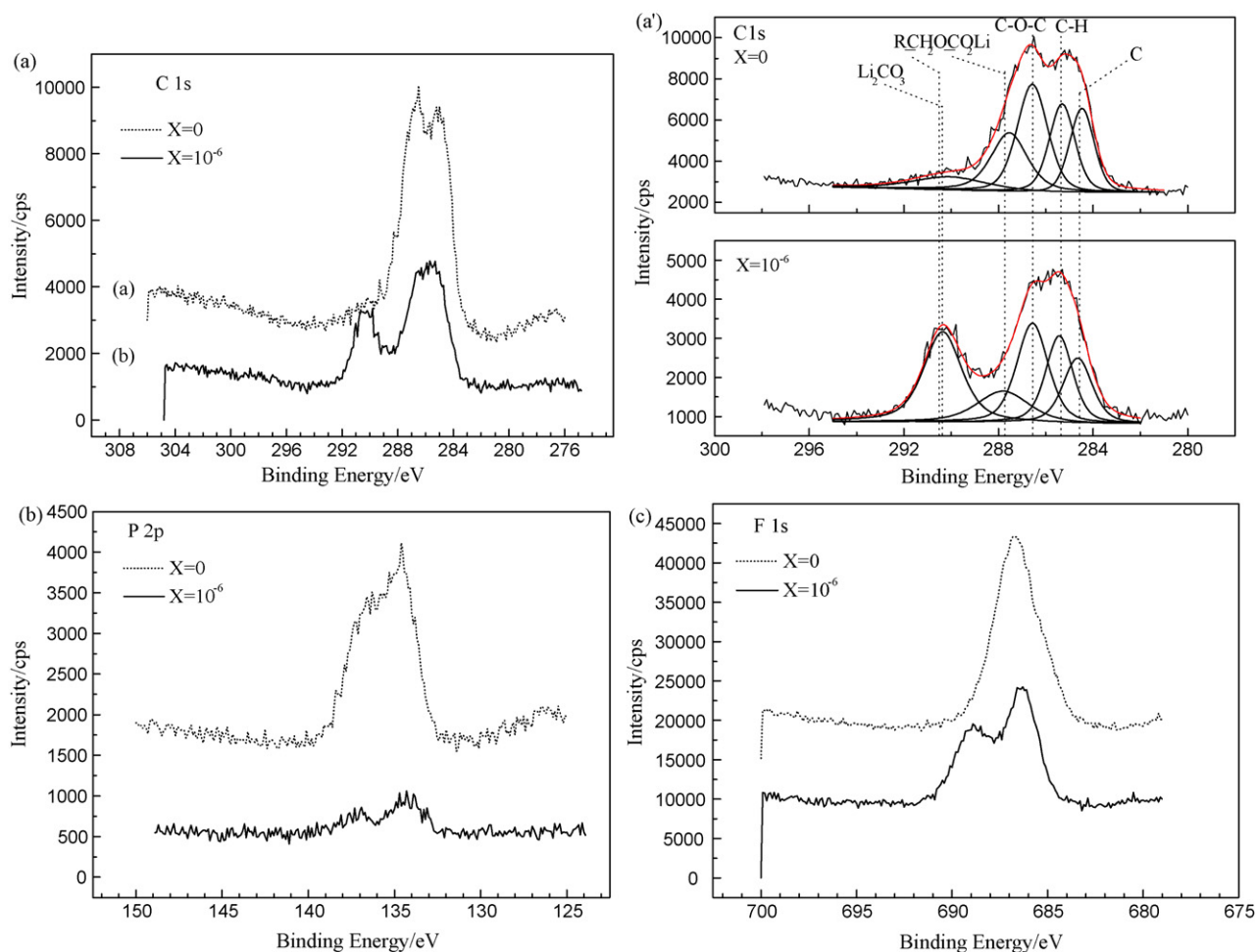


Fig. 6. C 1s, P 2p and F 1s XPS spectra of MCMB electrodes after the first cycle in 1 M LiPF_6 EC:DMC (1:1, vol) with 10^{-6} and without GCL: (a) and (a') C 1s; (b) P 2p; (c) F 1s.

electrode. Fig. 4a shows a typical SEM graph of the MCMB electrode without the electrochemical experiments, and Fig. 4b and c shows SEM graphs of the MCMB electrodes after the first charge–discharge process in electrolyte with and without GCL, respectively. Both the specimens of Fig. 4b and c are obtained from 100% delithiated MCMB electrodes to avoid the influence of Li. Compared with Fig. 4a, the surface of cycled MCMB electrodes was clearly covered a definite thickness layer, which was so-called SEI film. If we drew a comparison between Fig. 4b and c, we can find the SEI films were different, one (4b) was coarse and inhomogeneous distribution, and the other (4c) was a relatively smooth, compact and uniform film, which covered the surface of electrode.

The chemical components of the SEI film play a very vital role on determining the electrochemical performance. So following surface observations, we proceeded to SEI film components analyses used by FTIR and XPS. Fig. 5 indicates the results of FTIR spectra of MCMB electrodes cycled in electrolyte without and with GCL. As seen from Fig. 5, both (a) and (b) are basically similar: (1) the strong and broad peaks at 3438.5 cm^{-1} are belonging to the O–H stretching; (2) the weak peaks at $3000\text{--}2750\text{ cm}^{-1}$ are corresponding to the C–H stretching of alkanes; (3) the peaks at 1641 cm^{-1} ($\nu_{\text{as}}\text{C=O}$), 1401 cm^{-1} (δCH_3 , CH_2), 1315 cm^{-1} ($\nu_{\text{s}}\text{C=O}$), 1031 cm^{-1} ($\nu\text{C–O}$), 820 cm^{-1} (δOCO_2^-) are attributed to lithium alkyl carbonate (ROCO_2Li) species [18]; (4) the peaks at 1503, 1438, and 871 cm^{-1} are characteristic peaks of Li_2CO_3 [18]. So the main components of the SEI film all include (ROCO_2Li) and Li_2CO_3 for the electrolyte with and without GCL. Fig. 6 illustrates that C 1s, P 2p and F 1s XPS spectra of MCMB electrodes after the first cycle in EC-based electrolyte with and without GCL. When compared to the electrolyte without GCL, SEI film derived from GCL is less element (P, F) components, which indicate that the decomposition of LiPF_6 was inhibited by the presence of GCL. Through further analysis to the C 1s spectrum, we found that the component of SEI film derived from GCL has more Li_2CO_3 and less ROCO_2Li than that derived from the electrolyte without GCL, as a result, the SEI film has been more stable and more favorable to the intercalation and deintercalation of lithium ion, because the presence of considerable inorganic components has a beneficial effect on the stability of carbon anode [4], and the conductivity of Li_2CO_3 has higher than that of ROCO_2Li [24,25].

4. Conclusions

Through above discussion, we may draw a conclusion as follows:

Firstly, smaller volume amounts in the order of 10^{-6} GCL can efficiently improve the cyclic performance of MCMB electrode, and decrease the impedance of MCMB/Li half-cell.

Secondly, the results of cyclic voltammetry show that the GCL has higher reduction decomposition potential at about 2.1 V.

Thirdly, the SEI film derived from the electrolyte with GCL was more smooth and uniform than that form derived from the electrolyte without GCL.

Finally, the results of FTIR and XPS show that the main components of the SEI film all include (ROCO_2Li) and Li_2CO_3 for the electrolyte with and without GCL, and the SEI film derived from GCL is less element (P, F) components, and more Li_2CO_3 and less ROCO_2Li than that derived from the electrolyte without GCL.

So, the preferential reductive decomposition of GCL causes a smooth, uniform, stable and low-resistance SEI film, which leads to the excellent cyclability of MCMB electrode during long cycles.

References

- [1] E.J. Plichta, W.K. Behl, *J. Power Sources* 88 (2000) 192.
- [2] M.C. Smart, B.V. Ratnakumar, S. Surampudi, *J. Electrochem. Soc.* 149 (2002) A361.
- [3] M.C. Smart, B.V. Ratnakumar, L.D. Whitcanack, K.B. Chin, S. Surampudi, H. Croft, D. Tice, R. Staniewicz, *J. Power Sources* 119–121 (2003) 349.
- [4] J.O. Besenhard, M. Winter, J. Yang, W. Biberacher, *J. Power Sources* 54 (1995) 228.
- [5] D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, H. Yamin, *J. Electrochem. Soc.* 141 (1994) 603.
- [6] P. Arora, R.E. White, M. Doyle, *J. Electrochem. Soc.* 145 (1998) 3647.
- [7] M.C. Smart, B.V. Ratnakumar, S. Suramoudi, Y. Wang, X. Zhang, S.G. Greenbaum, A. Hightower, C.C. Ahn, B. Fultz, *J. Electrochem. Soc.* 146 (1999) 3963.
- [8] D. Aurbach, B. Markovsky, M.D. Levi, E. Levi, A. Schechter, M. Moshkovich, Y. Cohen, *J. Power Sources* 81/82 (1999) 95.
- [9] D. Aurbach, *J. Power Sources* 119–121 (2003) 497.
- [10] D. Aurbach, B. Markovsky, I. Weissman, E. Leci, Y. Ein-Eli, *Electrochim. Acta* 45 (1999) 67.
- [11] C. Wang, A. John Appleby, F.E. Little, *J. Electroanal. Chem.* 497 (2001) 33.
- [12] K. Takeno, M. Ichimura, K. Takano, J. Yamaki, *J. Power Sources* 142 (2005) 298.
- [13] A. Du Pasquier, F. Disma, T. Bowmer, A.S. Gozdz, G. Amatucci, J.-M. Tarascon, *J. Electrochem. Soc.* 145 (1998) 472.
- [14] G.V. Zhuang, P.N. Ross Jr., *Electrochem. Solid State Lett.* 6 (7) (2003) A136.
- [15] T. Takamura, H. Awano, T. Ura, K. Sumiya, *J. Power Sources* 68 (1997) 114.
- [16] N.J. Dudney, *J. Power Sources* 89 (2000) 176.
- [17] M. Ishikawa, H. Kawasaki, N. Yoshimoto, M. Morita, *J. Power Sources* 146 (2005) 199.
- [18] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, *Electrochim. Acta* 47 (2002) 1423.
- [19] K. Abe, T. Takaya, H. Yoshitake, Y. Ushio, M. Yoshio, H. Wang, *Electrochem. Solid State Lett.* 7 (12) (2004) A462.
- [20] H. Buqa, P. Golob, M. Winter, J.O. Besenhard, *J. Power Sources* 97/98 (2001) 122–128.
- [21] D. Aurbach, M.D. Levi, E. Levi, H. Teller, B. Markovsky, G. Salitra, U. Heider, L. Heider, *J. Electrochem. Soc.* 145 (1998) 3024.
- [22] C.H. Chen, J. Liu, K. Amine, *J. Power Sources* 96 (2001) 321.
- [23] K. Xu, *Chem. Rev.* 104 (2004) 4303.
- [24] D. Aurbach, A. Zaban, *J. Electrochem. Soc.* 141 (1994) 1808.
- [25] D. Aurbach, A. Zaban, *J. Electroanal. Chem.* 367 (1994) 15.