

## Effect of $\text{Li}_2\text{CO}_3$ additive on gas generation in lithium-ion batteries

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### Abstract

To elucidate the mechanism of gas generation during charge–discharge cycling of a lithium-ion cell, the generated gases and passive films on the carbon electrode are examined by means of gas chromatography (GC) and Fourier transform infrared (FTIR) spectroscopy. In ethyl carbonate/dimethyl carbonate and ethyl carbonate/diethyl carbonate 1 M  $\text{LiPF}_6$  electrolytes, the detected gaseous products are  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , etc. The FTIR spectrum of the surface of the carbon electrode shows bands which correspond to  $\text{Li}_2\text{CO}_3$ ,  $\text{ROCO}_2\text{Li}$ ,  $(\text{ROCO}_2\text{Li})_2$ , and  $\text{RCO}_2\text{Li}$ . These results suggest that gas evolution is caused by electrode decomposition, reactive trace impurities, and electrolyte reduction. The surface of the electrode is composed of electrolyte reduction products. When 0.05 M  $\text{Li}_2\text{CO}_3$  is added as an electrolyte additive, the total volume of generated gases is reduced, and the discharge capacity and the conductivity of lithium-ions are increased. These results can be explained by a more compact and thin ‘solid electrolyte interface’ film on the carbon electrode formed by  $\text{Li}_2\text{CO}_3$ , which effectively prevents solvent co-intercalation and carbon exfoliation. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Li-ion batteries; Additives; Gas generation; SEI;  $\text{Li}_2\text{CO}_3$

### 1. Introduction

Lithium batteries are noted for their high specific energy compared with other secondary batteries. Recently, rechargeable lithium-ion batteries with capacities of 1300–1900 mAh have been commercialized for some portable electronic devices such as camcorders, computers, and cameras [1]. In addition, lithium-ion and lithium-polymer batteries are being developed as power sources for electric vehicles to provide longer driving ranges, higher acceleration, and longer lifetimes [2,3].

Safety concerns have, however, limited the full utilization of lithium batteries [4–6]. Thus, battery safety is a key issue for the above applications. Electrolyte stability, in particular, is important for the entire safety of cells in practical use [7]. Therefore, one of the important factors in the development of long-life and safe lithium-ion batteries is the estimation of the decomposition and compositional change of electrolytes and electrodes during charge–discharge cycling. In addition, the electrode for which active surface area is increased unnecessarily, results in an overall increase of reaction with electrolytes and organic solvents. The reactions can result in an irreversible loss of anode capacity, and gradual oxidation

and consumption of electrolyte on the electrode. These effects, in turn cause capacity decline during cycling and an increased threat to battery safety by gas evolution [8].

Many researchers have attempted to understand the mechanism of the degradation of the electrolyte on the carbon electrode, and have suggested the formation of films on the surface of the carbon electrode during initial charging [9–12]. Ein-Eli et al. [13–15] published a series of studies on the formation of passive films in lithium batteries. Also, there has been considerable research into improving electrolyte systems for lithium batteries by the use of small amount of additives [11,16–18].

In this study, the electrolyte reduction and electrode decomposition are investigated by means of analysis of generated gases and passive films during repeated cycling of various electrodes and electrolyte systems, in order to elucidate the degradation mechanism of lithium-ion batteries. The main objective has been to reduce gas generation by using  $\text{Li}_2\text{CO}_3$  as an electrolyte additive.

### 2. Experimental

#### 2.1. Cells and electrode

Carbon electrodes were prepared from MCMB 25–28 material (~25  $\mu\text{m}$ , Osaka Gas Co.) by mixing the material

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with a solution of poly (vinylidene fluoride) (PVDF, Aldrich; 5 wt.%) dissolved in NMP (N-methyl 2-pyrrolidone, Aldrich). The slurry was then coated on a copper foil. The electrode was dried under vacuum at room temperature for 24 h.

Cathodes were prepared by mixing  $\text{LiCoO}_2$  ( $\sim 10 \mu\text{m}$ , Seimi Co.) powder with carbon black, and a solution of PVdF dissolved in a weight ratio of 90:4:6. These components were well mixed using a mortar and pestle, and then were coated on aluminum foil. The electrode was dried under a vacuum at  $120^\circ\text{C}$  for 24 h.

Electrolytes comprised a 1 M solution of  $\text{LiPF}_6$  in a 1:1 mixture (v/v) of ethylene carbonate (EC) and either diethyl carbonate (DEC) or dimethyl carbonate (DMC) (Merck, battery grade). A porous polypropylene film was used as the separator.

## 2.2. Electrochemical measurements

Charge–discharge measurements were performed with an Arbin cyler. Usually, the cells were cycled 50 times between 2.8 and 4.3 V at charging and discharging current densities of  $0.5 \text{ mA cm}^{-2}$  (C/5 rate), and terminated in the discharged state at 2.8 V.

The a.c. impedance measurements were carried out by means of an IM6 impedance analyzer (Zahner Elektrik). Impedance spectra were potentiostatically measured by applying an a.c. voltage of 5 mV amplitude over the frequency range 100 MHz–100 kHz after the electrode had attained equilibrium at each potential. All the potentials indicated here are based on the  $\text{Li/Li}^+$  electrode potential.

## 2.3. Instrumental measurements

Fourier transform infrared spectroscopy (FTIR) measurements of carbon electrodes were obtained by using Bomem

(MB-104) equipemnt. After cycling in a cell, the electrode was rinsed with dimethyl carbonate (DMC) to remove the salts, and then dried under vacuum at  $100^\circ\text{C}$  for 24 h. The surface of the carbon electrode was scratched with a stainless-steel knife. The powder was mixed with KBr and pelletized for IR measurement.

The generated gas in the cell was analyzed by gas chromatography. A Hewlett-Packard 5890 series gas chromatograph (GC), equipped with a flame ionization detector (FID), was used to detect hydrocarbons. A GOW-MAC GC, equipped with a thermal conductive detector (TCD), was used for composition analysis of the generated gases. For each sample, 0.5 ml (for TCD detector) and  $5 \mu\text{l}$  (for FID detector) of gas were injected for these analyses. After cycle test, the gases generated in the cells were drawn into a gas-tight syringe through the septum.

Experiments were performed with a two-electrode cell. In a lithium/carbon cell, the anode was lithium metal and the cathode was carbon. In a  $\text{Li/LiCoO}_2$  cell, the anode was lithium metal and the cathode was  $\text{LiCoO}_2$ . In a lithium-ion cell, the anode was carbon and the cathode was  $\text{LiCoO}_2$ .

All experiments were conducted at room temperature and in ambient conditions. Cell assembly was conducted under a dry argon atmosphere in a glove box.

## 3. Results and discussion

### 3.1. Gas generation

Tables 1 and 2 show the composition of generated gases during repeated cycling in ethylene carbonate/diethyl carbonate (EC/DEC) and ethylene carbonate/dimethyl carbonate (EC/DMC), EC/DEC and EC/DMC 1 M  $\text{LiPF}_6$  electrolytes. TCD was used to analyze the gas composition after 10, 30 and 50 cycles. The results show that the main

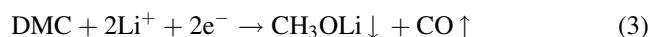
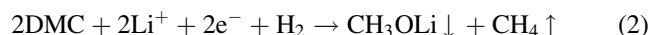
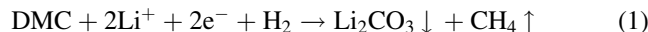
Table 1  
Composition of generated gases during repeated cycles in EC/DEC 1 M  $\text{LiPF}_6$  electrolyte

Generated gas	Li/LiCoO <sub>2</sub>			Li/C			C/LiCoO <sub>2</sub>		
	10 cycles	30 cycles	50 cycles	10 cycles	30 cycles	50 cycles	10 cycles	30 cycles	50 cycles
CH <sub>4</sub>	18.004	20.378	21.057	7.254	9.963	13.267	7.11	13.131	15.108
O <sub>2</sub>	0.014	0.010	0.007	–	–	–	0.018	0.015	0.010
CO	23.68	21.99	24.00	21.467	21.66	23.74	21.63	26.31	29.01
CO <sub>2</sub>	58.3	57.62	54.934	71.277	68.375	63.00	71.24	60.542	55.870

Table 2  
Composition of generated gases during repeated cycles in EC/DMC 1 M  $\text{LiPF}_6$  electrolyte

Generated gas	Li/LiCoO <sub>2</sub>			Li/C			C/LiCoO <sub>2</sub>		
	10 cycles	30 cycles	50 cycles	10 cycles	30 cycles	50 cycles	10 cycles	30 cycles	50 cycles
CH <sub>4</sub>	27.094	26.153	25.191	22.008	28.819	29.111	15.721	23.191	25.171
O <sub>2</sub>	0.018	0.014	0.011	–	–	–	0.018	0.016	0.01
CO	18.469	15.657	13.625	36.153	35.005	32.334	27.774	22.126	17.638
CO <sub>2</sub>	54.417	58.174	61.171	41.837	36.174	38.553	56.485	54.665	57.18

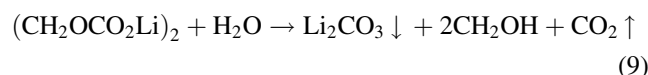
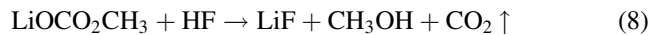
gases are  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{CO}$ . There is also a small amount of  $\text{O}_2$ . Aurbach et al. [14,15] reported that EC and DMC undergo a reduction reaction to form lithium alkyl carbonates,  $\text{CH}_4$  and  $\text{CO}$  on lithium metal. The generation mechanisms of  $\text{CH}_4$  and  $\text{CO}$  are considered to be as follows [24,27]:



As shown in Tables 1 and 2,  $\text{CO}$  and  $\text{CH}_4$  are mainly detected in the EC/DEC electrolyte and the EC/DMC electrolyte, respectively. These results are in good agreement with earlier studies which showed that the  $\text{CH}_4$  is generated mainly from DMC [14,15]. The data in Tables 1 and 2 also suggest that the main gaseous product is  $\text{CO}_2$ , irrespective of the choice of electrolyte solvent.  $\text{CO}_2$  gas can be generated by two different processes. One is the decomposition of the cathode material which, during overcharging, is understood to be [28]:



The other is the reaction via trace impurities ( $\text{HF}$  and  $\text{H}_2\text{O}$ ) in the electrolyte [29]:



Eq. (6) shows that  $\text{O}_2$  is generated as a result of decomposition of the overcharged cathode material. While, Eq. (7) shows that  $\text{CO}_2$  is produced as a result of the subsequent reaction of oxygen with the electrolyte. When  $\text{LiCoO}_2$  is not used as a cathode,  $\text{O}_2$  is not detected. Kumari et al. [28] have also claimed that  $\text{O}_2$  generation is due to the degradation of the cathode material.

Eq. (8) shows that  $\text{CO}_2$  is a final product on the lithium surface in electrolytes which contain  $\text{HF}$  as a contaminant (e.g. EC and DMC/DEC containing  $\text{LiPF}_6$ ) [16]. This result is essentially explained by acid–base reactions of  $\text{HF}$  with various basic lithium compounds in surface films. Also, the  $\text{CO}_2$  present may be formed by a secondary reaction of  $\text{ROCO}_2\text{Li}$  with trace water. The solutions unavoidably contain 20–30 ppm of water, which is sufficient (taking into account the large volume-to-Li-surface-area ratio) to affect markedly the surface films in the time scale of the experiments. Therefore, the generation of a large amount of  $\text{CO}_2$  is mainly due to the decomposition of the cathode material and the reaction of trace impurities.

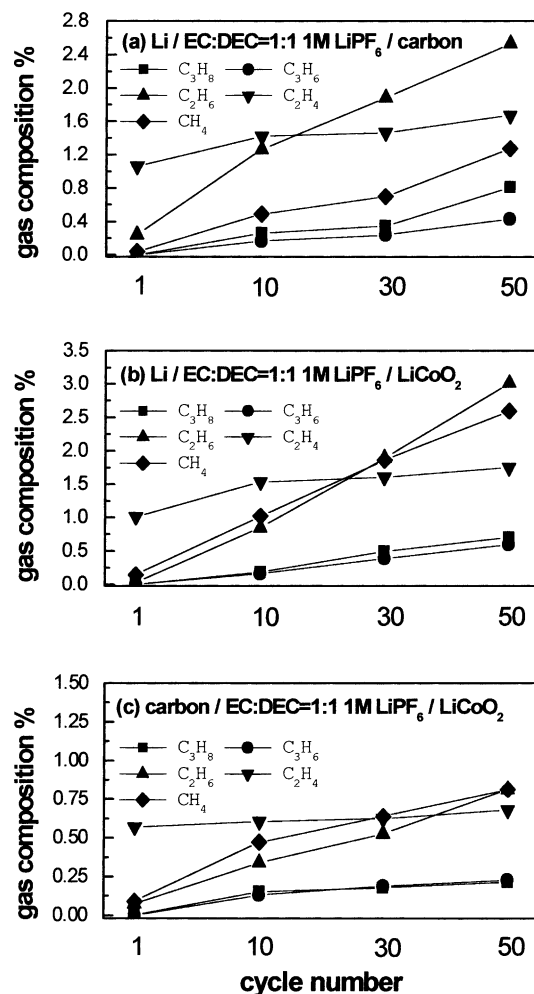
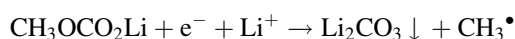
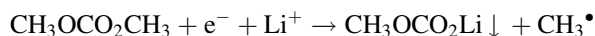
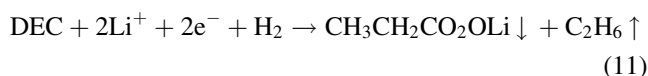
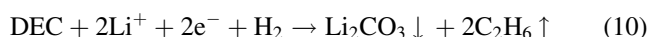


Fig. 1. Composition of detected gases during repeated cycling in the EC/DEC 1 M  $\text{LiPF}_6$  electrolyte (DEC set as 100).

The generated gases detected by FID during repeated cycling in EC/DEC and EC/DMC 1 M  $\text{LiPF}_6$  electrolytes are shown in Figs. 1 and 2, respectively. The value of y-axis represents the percentage composition of detected gases using DEC or DMC as an internal standard. As DEC or DMC gas produces its own gas, it is reasonable that DEC or DMC can be used as an internal standard. FID was used to detect generated hydrocarbon gases during the charge–discharge process. For the EC/DEC electrolyte, the gases are  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$ .  $\text{C}_3\text{H}_6$ , however, was not detected in the EC/DMC electrolyte. The generation mechanisms of the hydrocarbon gases, except for  $\text{CH}_4$ , are considered to be as follows [23,24,26,27].



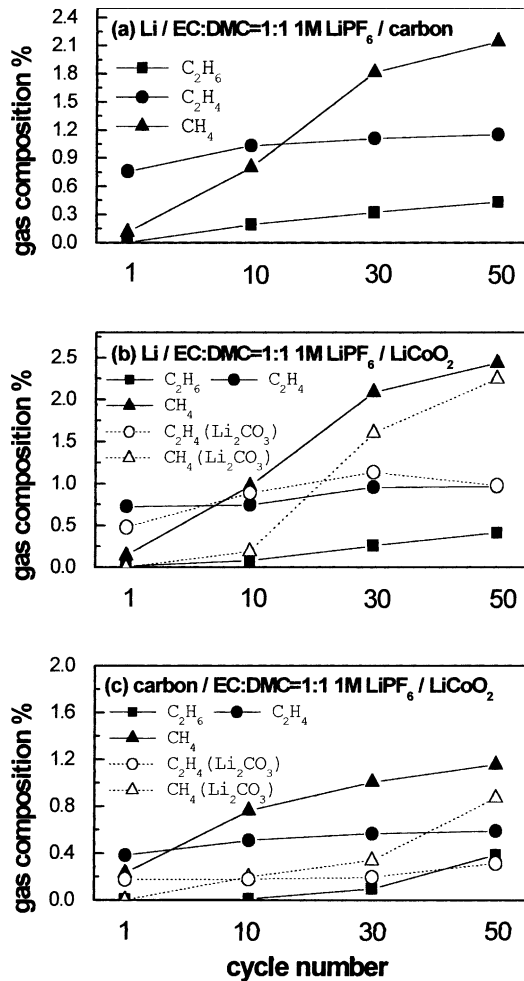
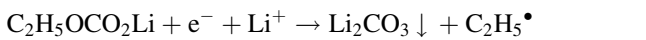
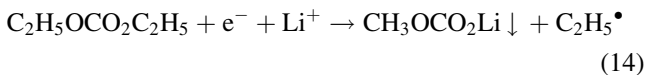
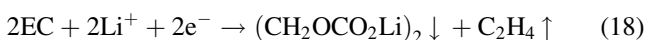
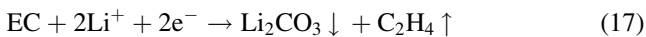


Fig. 2. Composition of generated gases during repeated cycling in EC/DMC 1 M LiPF<sub>6</sub> electrolyte with/without Li<sub>2</sub>CO<sub>3</sub> additive (DMC set as 100).



In Eqs. (1), (2), (10) and (11), hydrocarbons, except for C<sub>2</sub>H<sub>4</sub>, are produced from the reduction of DMC and radical reactions. C<sub>2</sub>H<sub>4</sub> is only generated by the reduction of EC, i.e. [17]



The data in Figs. 1 and 2 show that C<sub>2</sub>H<sub>4</sub> is the main gas product during the first cycle. While the total amount of detected gas continuously increases, the rate of C<sub>2</sub>H<sub>4</sub>

evolution decreases during repeated cycling, irrespective of the electrode under study. This result can be explained by prior reduction of EC on the carbon surface [19]. It is thought that the cyclic structure of EC can contact more closely the surface of the electrode than the linear structure of DEC or DMC. In addition, the polarity and dipole moments of EC are greater than those of DEC and DMC [19]. Comparing the lithium metal anode and carbon anode, greater amounts of gases are generated with the lithium electrode due to the high reactivity of this metal.

FTIR spectra obtained from carbon, taken from electrodes after 50 cycles in the salt solution (EC/DMC and EC/DEC 1 M LiPF<sub>6</sub>), are presented in Fig. 3. The spectra analysis is based on previous work [23,24,26,27]. In the EC/DEC 1 M LiPF<sub>6</sub> electrolyte, bands which correspond to Li<sub>2</sub>CO<sub>3</sub> ( $\nu = 1510\text{--}1450$  and  $875\text{--}860\text{ cm}^{-1}$ ), ROCO<sub>2</sub>Li, (ROCO<sub>2</sub>-Li)<sub>2</sub> and RCO<sub>2</sub>Li ( $\nu = 1640\text{--}1620$ ,  $1450\text{--}1400$ ,  $1350\text{--}1300$  and  $1100\text{ cm}^{-1}$ ) are observed. Similar results are also obtained for the EC/DMC electrolyte. On the basis of the spectral studies, the peaks are related to the reduction of electrolyte and lithium salts. This suggests that the passive film on the carbon electrode is formed by the reduction products of electrolyte, as shown in previous mechanisms.

### 3.2. Additive effect

According to the above mentioned gas generation mechanisms, Li<sub>2</sub>CO<sub>3</sub> is one of the electrolyte reduction products. From the reversible reduction reaction, it is thought that the amount of gas decreases on adding Li<sub>2</sub>CO<sub>3</sub> in the electrolyte. As already noted [20], it is well known that Li<sub>2</sub>CO<sub>3</sub> is produced as an electrochemical reduction product by bubbling CO<sub>2</sub> in the electrolyte. Unfortunately, however, the solubility of CO<sub>2</sub> in common lithium battery solvents is poor. Therefore, we directly added 0.05 M Li<sub>2</sub>CO<sub>3</sub> to the EC/DMC electrolyte to examine the effect of this additive.

The composition of the generated gases during repeated cycling in EC/DMC electrolyte and EC/DMC electrolyte containing 0.05 M Li<sub>2</sub>CO<sub>3</sub> is shown in Fig. 2. There are two important changes on adding Li<sub>2</sub>CO<sub>3</sub>. One is the virtual disappearance of C<sub>2</sub>H<sub>6</sub> gas. In Eq. (13), C<sub>2</sub>H<sub>6</sub> is formed by the CH<sub>3</sub><sup>•</sup> radical from the reduction of DMC. This suggests that adding Li<sub>2</sub>CO<sub>3</sub> to the electrolyte suppresses the formation of CH<sub>3</sub><sup>•</sup> radicals. The other change on adding Li<sub>2</sub>CO<sub>3</sub> is a reduction in the total amount of generated hydrocarbon gases. For an EC/DMC electrolyte system which contains 0.05 M Li<sub>2</sub>CO<sub>3</sub>, the total amount of generated hydrocarbon gases is 3.220% in a Li/LiCoO<sub>2</sub> cell, and 1.184% in a C/LiCoO<sub>2</sub> cell. Compared with the non-additive system, there is a decrease of 0.63% and 0.96% in the total amount of gases in the Li/LiCoO<sub>2</sub> cell and the C/LiCoO<sub>2</sub> cell, respectively.

The discharge capacity as a function of cycle number in EC/DMC electrolyte and EC/DMC electrolyte containing 0.05 M Li<sub>2</sub>CO<sub>3</sub> is shown in Fig. 4. A higher degree of discharge capacity and a long cycle-life are obtained with

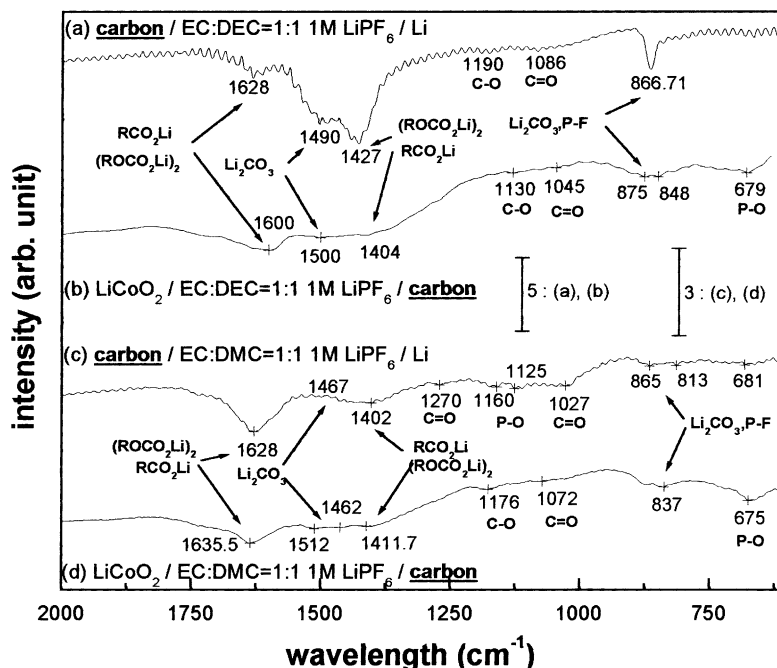


Fig. 3. FTIR spectrum of carbon electrode after 50 cycles in: (a) Li | EC/DEC 1 M LiPF<sub>6</sub> | carbon cell; (b) LiCoO<sub>2</sub> | EC/DEC 1 M LiPF<sub>6</sub> | carbon cell; (c) Li | EC/DMC 1 M LiPF<sub>6</sub> | carbon cell; (d) LiCoO<sub>2</sub> | EC/DMC 1 M LiPF<sub>6</sub> | carbon cell.

the electrolyte containing Li<sub>2</sub>CO<sub>3</sub>. The impedance spectrum for the first and tenth cycle is presented in Fig. 5. The first semi-circle, which corresponds to the interfacial impedance of the surface film formed on the carbon electrode, is observed [21–24]. The interfacial impedance for the EC/DMC electrolyte with Li<sub>2</sub>CO<sub>3</sub> is smaller than that for the EC/DMC electrolyte alone.

In general, when carbon is electrochemically charged with Li<sup>+</sup>-ions in an electrolyte, the intercalation reaction is accompanied by an irreversible process in which solution components are reduced on the carbon electrode. This behaviour has been said to form a ‘solid electrolyte interface’ (SEI) film [25] This prevents the co-intercalation

of solvent molecules into the graphite, a process that may result in increased irreversible charge consumption and sometimes even in graphite exfoliation. The reduction products include alkyl carbonate, lithium alkoxide, lithium alkyl carbonate, reduced anions, etc. Among them, it is well known that Li<sub>2</sub>CO<sub>3</sub> is an effective agent for forming SEI films on carbon electrodes [26]. When Li<sub>2</sub>CO<sub>3</sub> is used as an electrolyte additive, the passive film has already built up in Li<sub>2</sub>CO<sub>3</sub> before the reduction reaction occurs. Therefore, it effectively suppresses solvent co-intercalation reactions and graphite exfoliation. This is supported by the observation

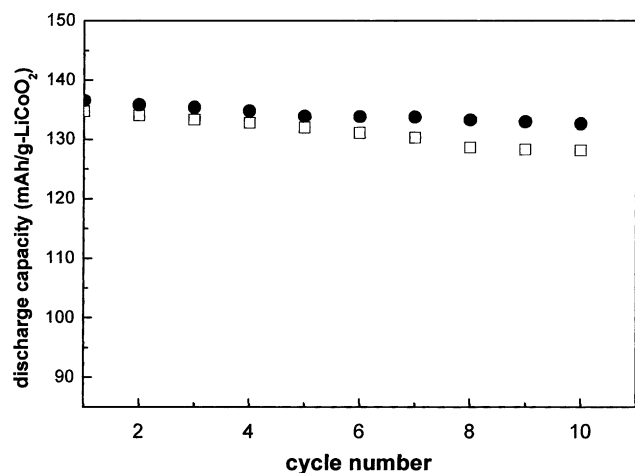


Fig. 4. Discharge capacity as function of cycle number of carbon | LiCoO<sub>2</sub> cell (□) EC:DMC = 1:1 1 M LiPF<sub>6</sub>; (●) EC:DMC = 1:1 1 M LiPF<sub>6</sub> + 0.05 M Li<sub>2</sub>CO<sub>3</sub>.

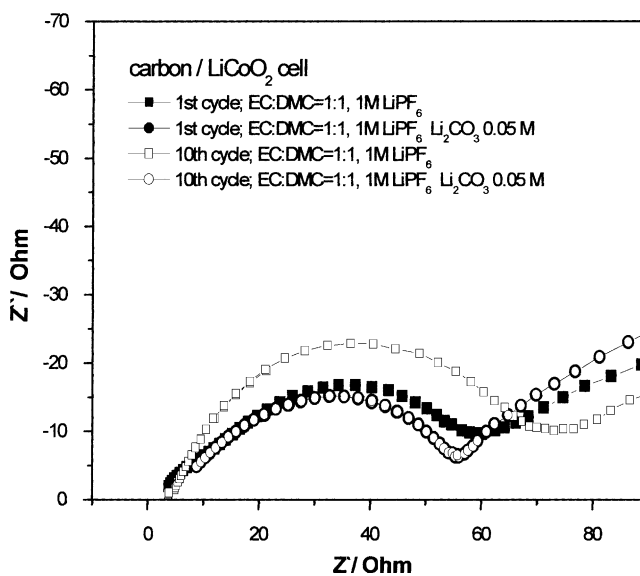


Fig. 5. Cole–Cole plots after first charge–discharge cycle of carbon | LiCoO<sub>2</sub> cell.

that the interfacial impedance (Fig. 5) for the EC/DMC electrolyte with  $\text{Li}_2\text{CO}_3$  is smaller than that for the EC/DMC electrolyte alone.

#### 4. Conclusions

From the results of gas chromatographic analysis, the generated gaseous products during repeated cycling of lithium-ion cells are  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$ . The composition of the detected gases is influenced by the nature of the electrolyte and the electrode. The main gaseous product is  $\text{CO}_2$  and is produced mainly by the decomposition of the cathode material and the reaction of trace impurities. The hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , etc.) and  $\text{CO}$  are produced by the reduction of DEC, DMC and EC. The generated gas compositions continuously increase during repeated cycling.

By adding 0.5 M  $\text{Li}_2\text{CO}_3$  as an additive,  $\text{C}_2\text{H}_6$  is not detected, because the formation of  $\text{CH}_3^\bullet$  radicals from the reduction of DMC is suppressed, and the total amount of generated gases is decreased. Also, cell performance is enhanced. These results can be explained by the formation of a more conductive SEI on the surface of the carbon anode, as confirmed by impedance measurements. Thus, it can be concluded that  $\text{Li}_2\text{CO}_3$  is an effective additive in reducing safety problems with lithium-ion batteries.

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