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ORIGINAL PAPER

EIS study of the influence of BrCl on the behavior of electrodes in Li/$SOCl_2$ cells

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Abstract The influence of BrCl on the impedance response of both the lithium anode and the carbon cathode in Li/$SOCl_2$ cells was studied. The impedance of the lithium anode increases with storage time while the addition of BrCl to Li/$SOCl_2$ cells decreases the impedance. However, the porous carbon cathode shows a small film resistance before discharge. The addition of BrCl to Li/$SOCl_2$ cells also decreases the impedance, especially for that part of the interface reaction resistance R_2. As a rule, the film resistance of the lithium anode decreases sharply during the early period of discharge, while that of the porous carbon cathode rises rapidly. It follows that the porous carbon cathode is the rate controlling electrode during discharge.

Keywords Li/$SOCl_2$ cell · BCX cell · BrCl · Electrochemical impedance spectroscopy

1 Introduction

Li/$SOCl_2$ cells have been widely applied in many fields such as military, aerospace, navigation, medical, downhole oilfield etc., due to their high energy density, wide operating temperature range and low self-discharge rate [1–4]. However, safety problems and voltage delay phenomena limit their further application. The voltage delay results from the formation of a LiCl film on the lithium anode surface, while the safety problems are more complicated.

The Li/$SOCl_2$ battery containing BrCl in the electrolyte is referred to as a BCX cell. BrCl not only greatly improves the safety and voltage delay performance but also increases the current output capacity of Li/$SOCl_2$ cells [5–7]. The open-circuit voltage is usually around 3.65 V. It increases to over 3.92 V when BrCl is added to the electrolyte [8, 9]. The increase in open-circuit voltage of BCX cells is attributable to the dissociation of BrCl to Cl_2 [5]. Liang [6, 7] and Abraham et al. [5] have reported that the addition of BrCl to Li/$SOCl_2$ cells not only results in higher open circuit voltage and larger capacity but also improves the low temperature capability and safety performance. Constant current discharge, cyclic voltammetry, UV, IR, and other techniques have been used in research on BCX cells [5–7]. Here the electrochemical behavior of BCX cells will be investigated by electrochemical impedance spectroscopy.

2 Experimental

One molar $LiAlCl_4$/$SOCl_2$ electrolyte was prepared in a three-neck flask in which $LiAlCl_4$ and $SOCl_2$ was refluxed for 10 h in the presence of lithium to remove the impurities and traces of water which may exist in the aprotic electrolyte. All measurements were carried out in a dry sealed glove box.

Electrochemical impedance spectroscopy was carried out in a three-electrode system in which one lithium electrode served as working electrode and another as reference and a porous carbon electrode served as counter electrode. The apparent surface area of the working electrodes was about 1.13 cm^2. EIS was carried out under open-circuit potential using an EG&G PARC M283 potentiostat and a PARC

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M1025 frequency response analyzer, supported by M398 software. The frequency range of the sinusoidal signals was 100 kHz–0.05 Hz and the amplitude was 5 mV. The impedance data were fitted by PAR 4.51 “Equivalent Circuit” software.

3 Results and discussion

3.1 Electrochemical impedance spectroscopy of the Li anode and the porous carbon cathode during storage

Nyquist plots of lithium anodes are shown in Figs. 1 and 2 for different storage times in $LiAlCl_4/(SOCl_2 + BrCl)$ and $LiAlCl_4/SOCl_2$ solution, respectively. The high-frequency semicircle in the figures corresponds to LiCl film formation on the lithium anodes [10]. The film resistance can be obtained from the corresponding semicircle diameter. The film resistance of the lithium anode initially increases with storage time and reaches a relative stable value. The addition of BrCl to the electrolyte inhibits the increase in the film resistance. The film resistance of the lithium anode in the BCX cell is 487 Ω after 9-day storage, while it reaches 1,300 Ω in the $Li/SOCl_2$ cell. The decrease in film resistance of the lithium anode caused by the addition of BrCl to the electrolyte facilitates the anode reactions.

Porous carbon cathodes are often used in $Li/SOCl_2$ or BCX batteries and they often act as the rate determining electrode [11–13]. As the electrochemical reduction of $SOCl_2$ takes place on the carbon cathode surface, the cathodic reaction products accumulated on the surface have a significant impact on discharge performance. The surface state of porous carbon also greatly influences the discharge performance.

As shown in Fig. 3, the Nyquist plot of the porous carbon cathode in $LiAlCl_4/(SOCl_2 + BrCl)$ solution consist of a high-frequency inductive reactance arc, a high-frequency capacitive reactance arc and a low-frequency capacitive reactance arc. The high-frequency inductive reactance arc may be related to the porosity of the carbon electrode. The high-frequency capacitive reactance arc corresponds to the film resistance and film capacitance of the carbon cathode, and the low-frequency capacitive reactance arc reflects the cathodic reduction process of $SOCl_2$ at the electrode/electrolyte interface [10]. As there are two time constants (ignoring the high-frequency inductive reactance arc) in Fig. 3, the equivalent circuit shown in Fig. 4 can be used to fit the plots, where R_1 represents the surface film resistance of the porous carbon cathode and R_2 the electrode/electrolyte interface resistance. The fitting results of Fig. 3 indicate that R_1 and R_2 are 25.61, and 46.12 Ω, respectively.

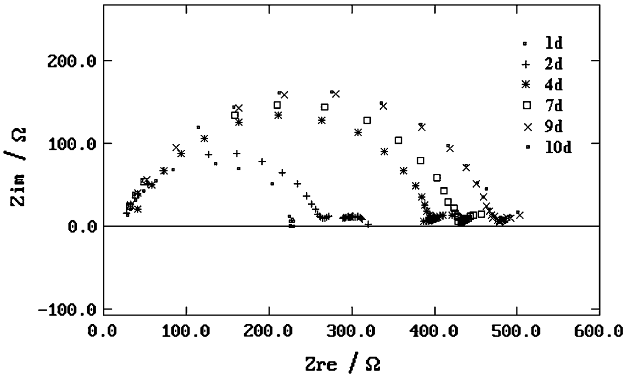

Fig. 1 Nyquist plots of the Li anode in $LiAlCl_4/(SOCl_2 + BrCl)$ solution for different storage times (“d” denotes “day(s)” in the figure)

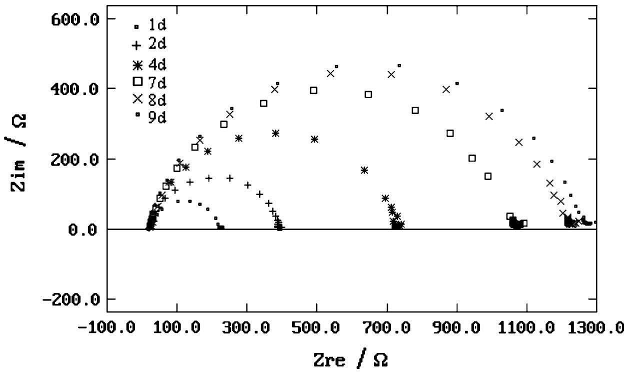

Fig. 2 Nyquist plots of the Li anode in $LiAlCl_4/SOCl_2$ solution for different storage times (“d” denotes “day(s)” in the figure)

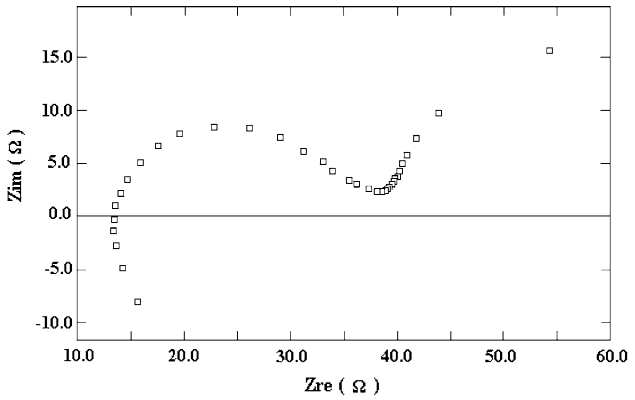

Fig. 3 Nyquist plots of the carbon cathode in $LiAlCl_4/(SOCl_2 + BrCl)$ solution

Nyquist plots of the porous carbon cathode in $LiAlCl_4/SOCl_2$ solution for different storage times are shown in Fig. 5. The surface film resistance changes only slightly with time, hence so does the long-term storage performance. The equivalent circuit in Fig. 4 was used to fit the impedance spectra of the 6-day-storage cell. The results

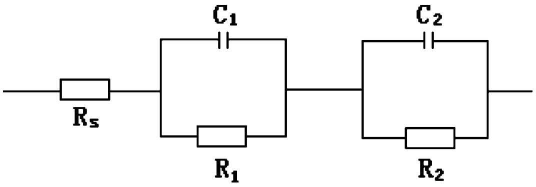

Fig. 4 Equivalent circuit of the carbon cathodes in the cell

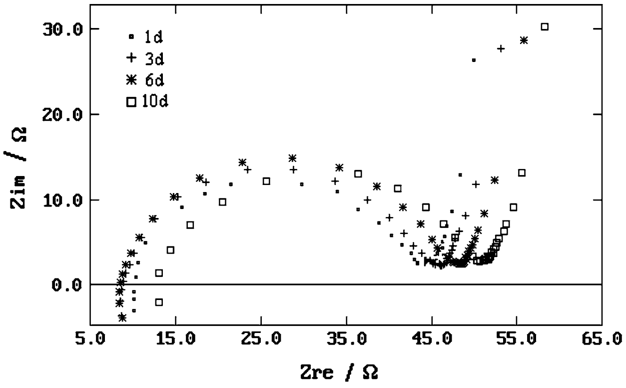

Fig. 5 Nyquist plots of the porous carbon cathode in $LiAlCl_4/SOCl_2$ solution for different storage times ("d" denotes "day(s)" in the figure)

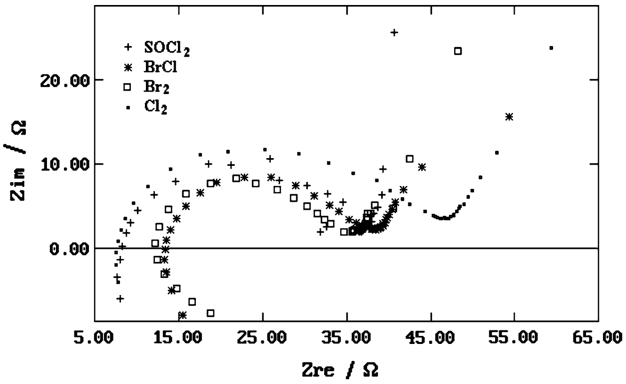

Fig. 6 Nyquist plots of the porous carbon cathode in $LiAlCl_4/SOCl_2$ solution with different additives

indicate that R_1 is 39.4 Ω and R_2 is 147.4 Ω, larger than the values of R_1 (25.61 Ω) and R_2 (46.12 Ω) with the addition of BrCl. The addition of BrCl decreases the R_2 value which corresponds to the electrode/electrolyte interface resistance of $SOCl_2$ reduction, and is thus beneficial to discharge performance. As has been shown in Fig. 6, for the porous carbon cathodes in $LiAlCl_4/SOCl_2$, $LiAlCl_4/(SOCl_2 + BrCl)$, $LiAlCl_4/(SOCl_2 + Br_2)$ and $LiAlCl_4/(SOCl_2 + Cl_2)$, all the additives including BrCl, Br_2, and Cl_2, are effective in decreasing the interface resistance of $SOCl_2$ reduction; among them BrCl is the best.

3.2 The change of impedance of the electrodes during discharge

The impedance of the lithium anode decreases rapidly during discharge, as shown in Fig. 7a. The film resistance of the lithium anode decreases quickly from 155.8 Ω before discharge to 27.5 Ω after 3 h discharge since Li^+ ions as the anode reaction product pass through the passive film on the lithium electrode in the process of discharge, causing destruction of the passive film and a decrease in film resistance. However, the film resistance of the lithium anode gradually increases with further discharge, as shown in Fig. 7b, the blowup of the high frequency region in Fig. 7a. The gradual increase in film resistance of the lithium anode is related to deposition of reaction products on the lithium anode surface during discharge.

The film resistance of the porous carbon cathode changes slightly during storage, as shown in Fig. 5, due to the low self-discharge rate. However, the cathode impedance increases significantly during discharge, because the products of the cathodic reaction rapidly increase and block the pores on the carbon surface. Figure 8 shows the Nyquist plots of the porous carbon cathode in a BCX cell during discharge, indicating that the surface resistance of

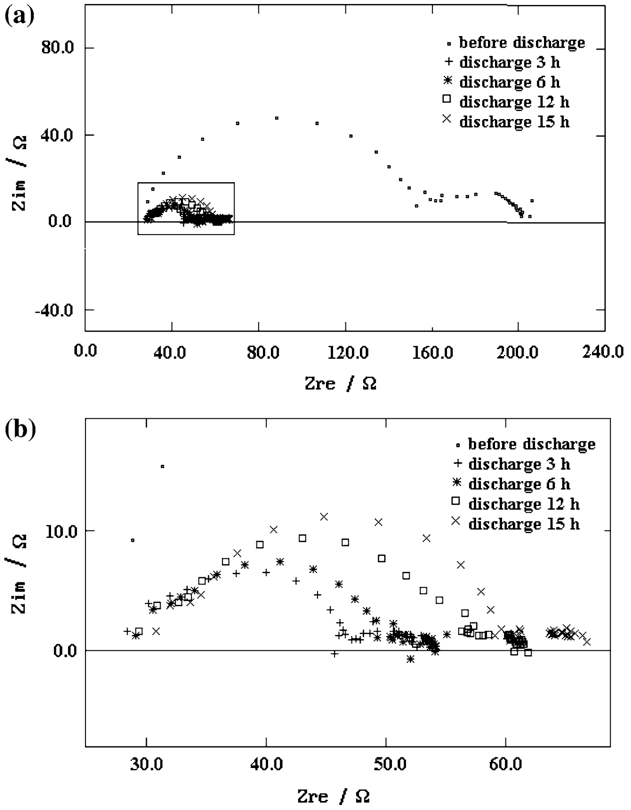

Fig. 7 Nyquist plots of the Li anode in a BCX cell during discharge at 3 mA (the plots in "**b**" are the blowups of the high frequency region in "**a**")

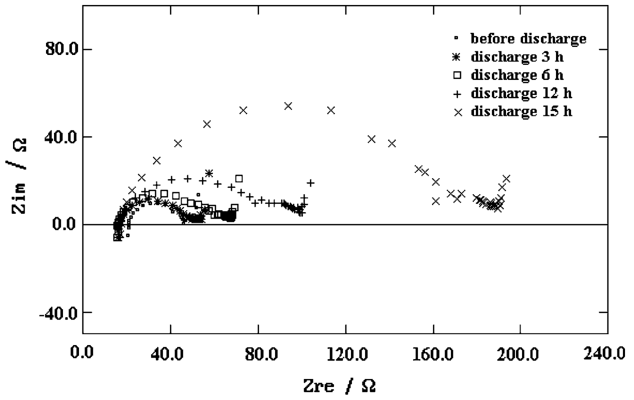

Fig. 8 Nyquist plots of the porous carbon cathode in a BCX cell during discharge at 3 mA

the carbon cathode increases sharply. The fitting results show that the film resistance of the carbon electrode is 25.6 Ω before discharge, but reaches 189.7 Ω after 15 h discharge, which is about 7 times larger than the value before discharge. Therefore, the carbon cathode turns out to be the rate determining electrode in a BCX cell.

4 Conclusions

(1) The impedance of the lithium anode increases with storage time as a result of surface film formation. BrCl added to the electrolyte effectively inhibits the increase in film resistance. The film resistance of the lithium electrode in a BCX cell is 487 Ω, while it reaches 1,300 Ω in a $Li/SOCl_2$ cell without BrCl after 9 day storage.

(2) In contrast to the lithium electrode in the $Li/SOCl_2$ cell, the surface film resistance of the porous carbon cathode is relatively small before discharge and changes slightly with storage time. The addition of BrCl decreases both the film resistance R_1 and the interface reaction resistance R_2, which is beneficial to cell discharge.

(3) The film resistance of the lithium anode in BCX cells decreases rapidly in the early period of discharge, from 155.8 Ω before discharge to 27.5 Ω after 3 h discharge. However, it gradually increases with further discharge due to deposition of reaction products on the Li surface.

(4) The film resistance of the porous carbon cathode in a BCX cell increases during discharge from 25.6 Ω before discharge to 189.7 Ω after 15 h discharge; thus the carbon cathode turns out to be the rate controlling electrode.

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