Electrochemical Impedance Spectra and State-of-charge Analysis of Lithium—Thionyl Chloride Primary Batteries

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Abstract: The EIS of $Li/SOCl_2$ batteries (3.6V/1.2Ah) were measured at various SOC in the frequency range 20 kHz ~ 5mHz. It was found that the EIS altered with strong regularity during the discharge, which externalized the two semicircles becoming bigger gradually as well as the secondary semicircle drifting upwards gradually. It is possible to use the EIS alter characteristics for estimating the cell's SOC. The most informative parameters for the SOC test in the region 40% ~ 0% are the ImZ^*, $\log(Z^*)$ and phase θ^* on the extreme point of an EIS.

Key words: $Li/SOCl_2$ battery; state-of-charge (SOC); Electrochemical Impedance Spectra (EIS)
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The problem of the predicted available remaining capacity monitoring by a. c impedance is an important aspect of the primary and secondary cells[1-3]. With the assumption that the anode lithium electrode melts uniformly during discharge with a smooth surface and its contribution to the impedance of cells is not great and may be ignore. In this paper, the cells' EIS were tested at active state after each discharge without the effect of the passive film on the anode lithium electrode.

1 Experimental

The electrolyte of the $Li/SOCl_2$ cells was 1.2 mol/L $LiAlCl_4/SOCl_2$ and about 5% SO_2. The EIS measurements were performed on an Autolab Electrochemical Station with 5mV amplitude at open potential after various amounts of charge had been removed. The cells discharged on 330 Ω load. At least 4 h was allowed to elapse for diffusional processes within the cell to become completed before the commencement of the a. c experiment. And the basic impedance parameters were then analysised with the cells SOC, including the Ohmic resistance R_Ω, phase θ^*, the $\log(Z^*)$, as well as the imaginary ImZ^* and real ReZ^* constituents of the impedance at the extreme point of EIS.

2 Results and discussion

2.1 The EIS of the cells at different SOC

In fig1, the impedance spectra at the various SOC differed throughout the whole rang, 0 to 100%. At 100% SOC, the large semicircle corresponds to the resistance of the passive film formed on the surface of lithium. And the effect of passive film was not detected mostly at 97% ~0% SOC. The passive film was broken-down when the current passed through the anode and cathode electrodes of the cell. And so the diameter of the semicircular on high frequency minished considerably at first. The dual semicircular shape was maintained more or less throughout the region. With the SOC decreasing, the second semicircular became bigger and bigger, as well as shifted upwards gradually. The characteristic of the first and second semicircular on impedance spectra gives one chance to use this two semicircular for predicting SOC. The enlarged part on high frequency range is shown as the little figare in Fig. 1. The way the impedance characteristics alter brings a chance to use the impedance phase θ^*, ImZ^* and $\log(Z^*)$ for determining the SOC of lithium thionyl chloride.

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2.2 The dependences of the impedance parameters on cell's SOC

As shown in Fig 2, the dependences of the impedance log(Z*), ImZ* and Phase θ* are better correlators of the cell's SOC. And there is an obvious common point from the dependences of ImZ*, log(Z*) and phase θ* that this three impedance parameters became increasing considerably when the cell's SOC is ≥ 40% (about 480 mAh capacity). And in this interval of 40% ~ 0%, the cell's SOC is possible to estimate use ImZ*, log(Z*) and phase θ* at the extreme point of impedance spectra. At ≤ 40% SOC, the cell's SOC is difficulty to determine due to the absence of obvious change in the informative parameters. Here the dependence differs largely from paper[4-5], which is possible due to the different manufacture and ingredient of the impedance parameters in this experiment.

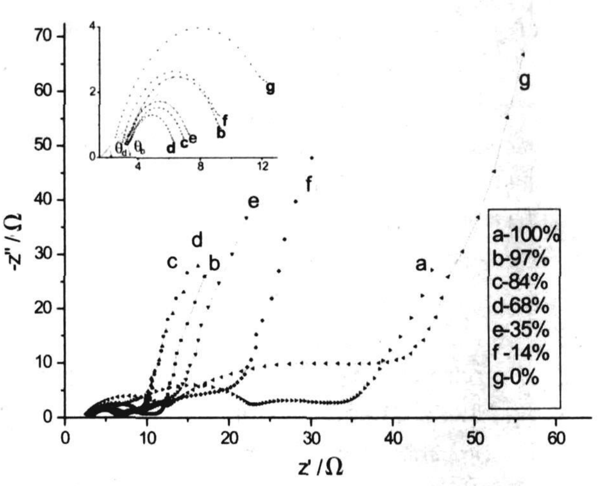

Fig 1　The chang regulation of EIS during dischage process

3 Conclusions

The impedance spectroscopy may, in prince, be used for estimating SOC of a Li/$SOCl_2$ battery. To do this, the passive film must be removed at first. And the impedance ImZ*, log(Z*) and Phase θ* on the extreme point of an impedance spectrum can be employed for the battery as the informative parameters for determining the cell's ≤ 40% SOC.

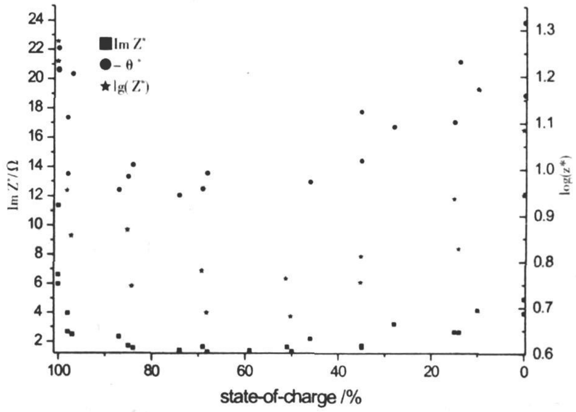

Fig 2　Dependences of impedance parameters on SOC

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一次锂/亚硫酰氯电池电化学阻抗谱与荷电状态

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摘　要：对 Li/$SOCl_2$ 实体电池不同荷电状态下电池电化学阻抗谱测试，结果表明，电池阻抗谱变化有很好的规律，主要体现在阻抗谱中两个圆弧的先较小后增大。这就有可能根据电池 EIS谱局部变化特征来预测电池的荷电状态。在电池荷电状态≤ 40%时，其有效预测参数为阻抗谱高频端圆弧最高点对应的 ImZ*，log(Z*)及相角 θ*。

关键词：Li/$SOCl_2$ 电池；荷电状态 (SOC)；电化学阻抗谱 (EIS)

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