ABSENCE OF CONVECTIVE MASS TRANSPORT IN GEL ELECTROLYTES

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Introduction

Gel polymer electrolytes were introduced in the lithium battery technology. Among their features, the almost total immobility is rather important. Moreover, the gels contain a solution of cations and anions both of them influenced by electrolytic migration. Therefore, the transference number of the electroactive ion (for example, lithium ion in lithium batteries) is fairly below unity. For the PMMA-PC-$LiClO_4$ gels we have found the transference number t_{Li} = 0.3 to 0.4 [1,2]. Moreover, we suggested to use the electrodeposition of cadmium as a model system for the investigation of processes in negative lithium electrodes. The aim of this paper is the explanation of rapid decay of current after negative potenetial had been applied on the electrode. The hypothesis was created that the immobility of the gels prevents any natural convection and only diffusion-controlled reactions are involved.

Experimental

PMMA-PC based gels were prepared so that a 0.1 M solution of perchlorates (with respect to perchlorate ions) was used. A series of gels was prepared in which part of cadmium was substituted by equivalent of lithium salt. The degree of replacement was chosen equal to 0%, 30%. 50% and 70%.

At the beginning, the impedance spectrum of the system was recorded. Then a voltammetry towards negative potentials was performed. Finally, the impedance spectrum was recorded again.

Results and Discussion

The example of voltammetry (in the case of 100% CD gel) is shown in Fig. 1.

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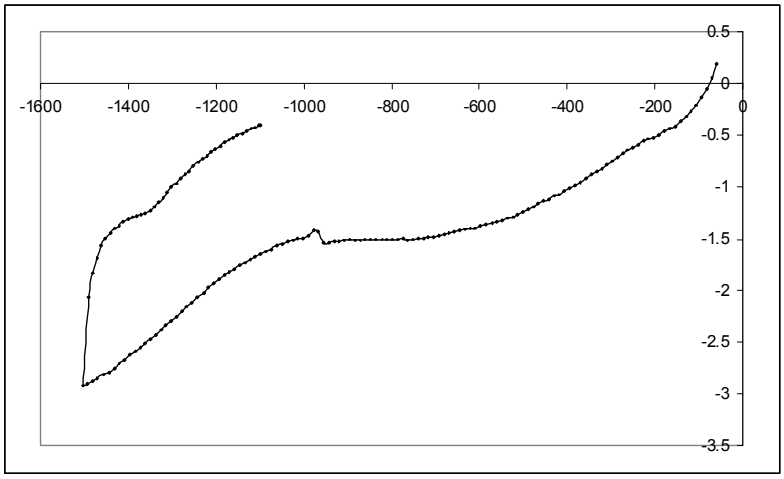

Fig. 1 *Voltammetry of cadmium deposition from 100% Cd gel.*

Rather fast decay of current at -1200 to -1400 mV is visible there. The impedance spectrum before and after the cadmium deposition from 100% Cd gel is shown in Fig. 2.

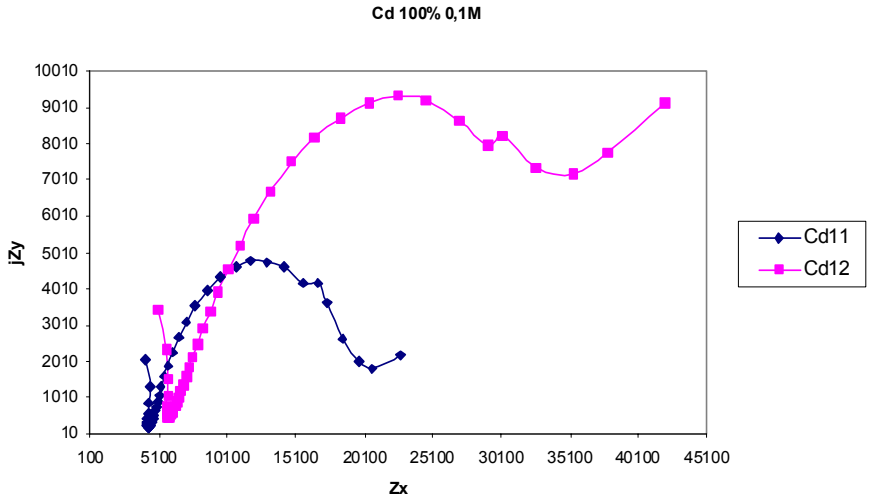

Fig. 2 *Impedance spectrum of a fresh and depleted gel (100% Cd).*

The depletion of the gel yields in an increase of series resistance at high frequencies, the increasing impedance of a R-C loop and in the shift of low frequency diffusion controlled part of the spectrum to higher impedance values.
For comparison, the impedance spectra of a gel containing 30% CD and 70% Li is given in Fig. 3.

In comparison to Fig. 2, neither ohmic resistance nor the R-C loop are shifted so drastically due to the presence of inert lithium salts and to the presence of residual gel conductivity after removal of cadmium from the surrounding of the electrode.

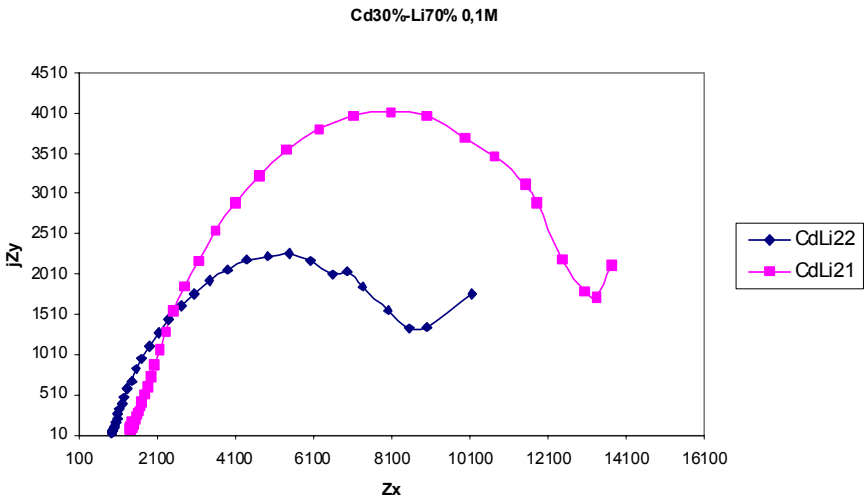

Fig. 3 *Impedance spectrum of a fresh and depleted gel (30% Cd).*

Conclusions

Apparently, the depletion of gel on electroactive species seems unpleasant and may cause difficulties in lithium gel batteries. This has been studied by numeric simulation by Newman et al. [3] for a complete cell. It is quite important to prepare electrolytes with possibly high transference number of lithium ions. This can be achieved probably using salts of lithium with as large anions as possible. A polymeric anion soluble in PC could be one of possibilities.

Acknowledgements

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