

Metal deposition in absence of convective mass transport in polymer gel electrolytes: A model of lithium anode in batteries

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Anotation:

The depletion of PMMA gel polymer electrode containing a binary electrolyte (cadmium perchlorate $\text{Cd}(\text{ClO}_4)_2$ in propylene carbonate PC) has been investigated. Impedance spectra were measured before and after recording a voltammogram of cadmium electrodeposition. The increase of electrolyte resistance, of polarisation resistance, and capacity component were evaluated. All these parameters indicate a strong depletion, which is known in Li polymer secondary cells, and which was lowered if a part of cadmium perchlorate was replaced by corresponding amount of LiClO_4 as an indifferent electrolyte.

Zkoumáno bylo ochuzení PMMA gelové elektrody obsahující binární elektrolyt (chloristan kademnatý $\text{Cd}(\text{ClO}_4)_2$ v propylen karbonátu PC). Impedanční spektra byla měřena před a po záznamu voltamogramu při elektrodepozici kadmia. Vyhodnoceno bylo zvýšení odporu elektrolytu vlivem polarizačních ztrát a kapacity jednotlivých komponent. Všechny tyto parametry ukazují silný úbytek iontů, který je známý v Li polymerních sekundárních článcích, a který byl snížen, když část chloristanu kademnatého byla nahrazena odpovídající částkou chloristanu lithného LiClO_4 jako indiferentního elektrolytu.

INTRODUCTION

Gel polymer electrolytes were introduced in the lithium battery technology one decade before. Among their features, the almost total immobility is rather important. These 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, t_{Li}) is fairly below unity. The importance of this value for lithium batteries containing quasi solid gel electrolytes was emphasized for example in papers [1, 2]. Transference numbers as low as 0.5 or even less were found in the paper by How and Siow [3] for an electrolyte containing LiClO_4 in ABS/PMMA based gel. Apparently zero or even negative value of t_{Li} were reported by Christie, Christie and Vincent [4]. Low transference number of cation was found in a similar gel based on PMMA and magnesium triflate by Ferry *et al.* [5].

Numerous reports concerning transference numbers in gel polymer electrolytes can be found in literature, both based on theoretic considerations and direct experimental measurements. They are based on Hittorf method [6], on the mobility obtained by NMR [7] or electrophoretic NMR [8] and on the comparison of initial and steady currents using two completely polarized (blocking) electrodes (for example, Hou and Siow [3], Christie *et al.* [4] or Kumar and Munichandraiah [5]). Other methods were developed by Ferry *et al.*, by Xu and Farrington [9]. For the PMMA-PC- LiClO_4 gels we have found the transference number $t_{\text{Li}} = 0.3$ to 0.4 (cit. [10-12])

from *e.m.f.* measurement of concentration cells containing the lithium and tetramethylammonium perchlorates with constant perchlorate concentration (*i.e.*, constant ionic strength) and lithium amalgam electrodes.

The gel polymer electrolytes are evidently immobile, which is visible at first sight. On contrary to liquid electrolytes, the gel electrolytes are transport of ions in gel polymer electrolytes is possible therefore only thanks to electrolytic migration and diffusion and the value of transference number can be of considerable influence on any application of a solid gel electrolyte. For example, the charging of a negative electrode in a lithium ion battery is always connected with the depletion of the electrolyte adjacent to the active surface of the negative electrode and yields in a sharp decrease of current. This has been studied by Newman and coworkers [13] by means of digital simulation of transport processes in a lithium cell and the voltage loss in the electrolyte can reach considerable values and also by Newman and coworkers empirically in paper [14].

Similarly to our previous papers [15, 16], we suggested to use the electrodeposition of cadmium as a model system for the investigation of electrolyte depletion in the surrounding of the negative lithium electrodes. The aim of this paper is the explanation of rapid decay of current after negative potential had been applied on the electrode. This is demonstrated in Fig. 1 where the decay of current at cathodic polarization by a voltage -1 V is plotted. The current drops rapidly from initial value asymptotically to zero. Due to simple experimental arrangement, it is

difficult to plot current as a function of time $t^{1/2}$ what would be expected for a process controlled just by diffusion.

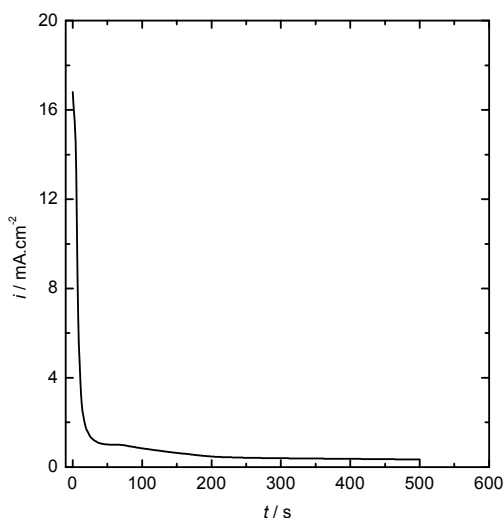


Fig. 1: The decay of current after imposing potential -1V on a Cu electrode in 100% PMMA-PC-Cd(ClO₄)₂ gel (against Cu counterelectrode)

However, this experiment illustrates the problem of cathodic electrodeposition of metal (*i.e.* charging of a negative electrode of lithium battery) sufficiently. A hypothesis was created that the immobility of the gels prevents any natural convection and only reactions controlled by diffusion and migration are involved.

The aim of this work was to create a model of metal deposition from a immobile electrolyte in which no convective mass transfer is possible. We have also verified how the presence of an electrochemically inert cation can diminish the unwanted current decay in quasisolid gel electrolyte. Therefore we used mixtures of Cd and Li salt in equal concentration for this purpose. The gels containing cadmium salts have been proved as quite effective in gel electrolyte research [17].

EXPERIMENTAL

PMMA-PC based gels were prepared so that stock solutions of 0.1M lithium and/or cadmium perchlorates in PC (with respect to perchlorate ions) were used. A series of gels was then 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 %. The method of gel preparation was described in our previous papers [21, 22]. The thickness of the gel layer was from 1 to 2.5 mm.

Copper foil of surface area 1 cm² was used both as working and counter electrodes in a two – electrode arrangement. The process on negative electrode is based on the deposition of metallic cadmium while on the counter electrode, the double layer charging,

irreversible oxidation of propylene carbonate and oxidation of copper must be taken in account.

At the beginning, the impedance spectrum of the system was recorded in the frequency range from 22 kHz down to 0.1 Hz at the potential 0.0 V in a two-electrode. Then, a voltammetry towards negative potentials was performed at scan rate 0.01 V.s⁻¹. Finally, the impedance spectrum was recorded again immediately after the voltammogram had been recorded and the electrolyte had no time to reestablish equilibrium concentration field and the impedance spectrum reflects the non-stationarity in a way as a “fingerprint” of an exhausted system.

Potentiostat Autolab (ECONCHEMIE, The Netherlands) and its software were used for all experiments.

RESULTS AND DISCUSSION

An example of two voltammograms is plotted in Fig. 2. One was recorded in a gel containing cadmium only, while the second one was found using a gel containing 70 % of Cd salt only and 30 % of Cd was replaced by corresponding amount of lithium salt.

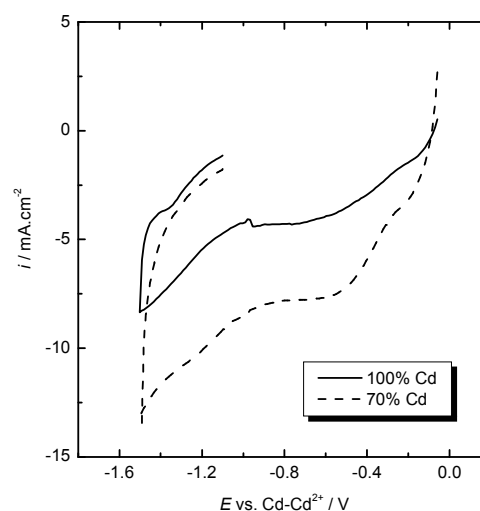


Fig. 2: Voltammetry of 100% gel (solid line) and 70% Cd containing gel (dash line)

Rather fast decay of current at -1200 mV to -1400 mV is visible there. The current is higher if the Cd ions are partly replaced by lithium ions in the gel containing 70 % Cd only, in comparison to 100 % Cd gel thus indicating the inhibitive action of the pure binary electrolyte and its depletion on cadmium ions in the vicinity of the negative electrode.

The impedance spectrum before and immediately after the cadmium deposition from 70% Cd gel is shown in Fig. 3 as an example. The equivalent circuit used for the parametrisation of the spectrum is given there as a curved line.

The recording of the voltammetric curve was accompanied by the depletion of the gel electrolyte in nearest vicinity of working electrode. 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. Exact analysis of the results by the equations used for an equilibrated system is impossible as the composition of the electrolyte is changed by previous metal deposition.

For elucidation of the process parameters, an equivalent circuit containing several components was used. First, there is a series resistance R_1 of the bulk electrolyte. Second, a parallel couple of a resistance R_2 and a C.P.E. (constant phase element) type element Q should be connected in series with the first one. Finally, we can observe a trace of another Warburg component W at the low frequency end of the spectrum (close to 0.1 Hz). Unfortunately, the spectrum had to be recorded down to 0.1 Hz only for technical reasons. Hence, the Warburg component was estimated with a considerable uncertainty (ca. 10 % – 15 %). The Boucamp software delivered by ECOCHEMIE – AUTOLAB potentiostats was used for their estimation. The results are given in Table 1. The description of the equivalence circuit is inserted into Fig. 3.

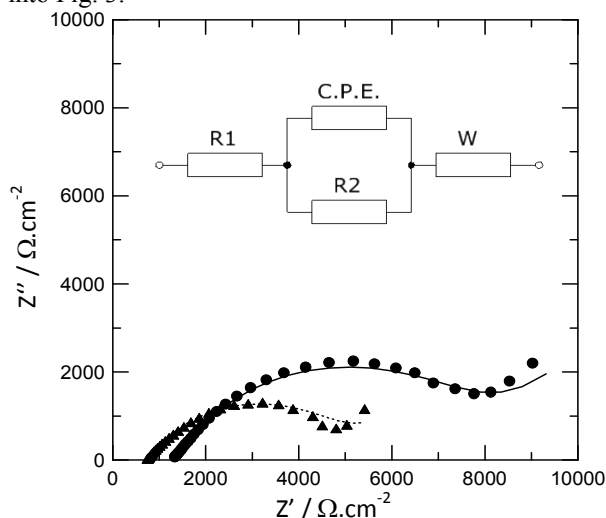


Fig. 3: Nyquist plots of a gel containing 70 % Cd measured at open circuit voltage (filled triangle: initial spectrum; filled circle: spectrum after recording a voltammogram). The equivalent circuit used for data description is inserted

Tab. 1: Parameters of the equivalent circuits of fresh gel and gel after recording a voltammetric curve. Meaning of symbols: R_1 – resistance of the electrolyte, R_2 – polarization resistance, Q_1 – C.P.E. similar to the capacity (equal to $Q = Q_1 \cdot \omega^k$, $k \approx 0.7 - 0.75$), W – Warburg admittance controlled by ionic movement

Before voltammetrical measurement				
w (Cd(ClO ₄) ₂) (mol. %)	R_1 (Ω.cm ⁻²)	R_2 (Ω.cm ⁻²)	$10^7 Q_1$ (S.cm ²)	$10^3 W$ (S.cm ²)
100	1530	5790	1.19	4.37
70	267	1520	2.28	4.84
50	540	1410	1.85	3.87
30	325	2700	1.36	2.37
After voltammetrical measurement				
w (Cd(ClO ₄) ₂) (mol. %)	R_1 (Ω.cm ⁻²)	R_2 (Ω.cm ⁻²)	$10^7 Q_1$ (S.cm ²)	$10^3 W$ (S.cm ²)
100	2019	10990	0.09	0.46
70	464	2282	1.36	1.54
50	886	2408	0.29	1.90
30	506	4278	1.36	2.67

Undoubtedly, a depletion of the electrolyte in nearest vicinity to working electrode occurs. The gel electrolyte is macroscopically immobile and does not allow any streaming or other convective mixing. The fast decay of the current at constant voltage, which was depicted in Fig.1, is rather similar to the results described in Fig. 1 of the paper published by Croce et al. [18] for the case of lithium perchlorate solution in acetonitrile. However, the current in our case decreased almost to zero and no transference number was available from the curve by the procedure described in mentioned paper. Apparently, this was caused by polarization effects on both electrodes or the method is not applicable in our case for some other reason. For comparison, we can consider the value of transference number for lithium which we found earlier [10-12, 15-16]; its value was equal to 0.4 approximately. Qualitatively, we observed similar values by the same method for cadmium ions [23]. As we observed earlier [10-12, 15-16], the electrodeposited cadmium has much finer morphology than that of deposition from liquid propylene carbonate and does not separate whiskers or large particles. This, too, may be the result of a deposition from an electrolyte with very low cadmium content.

Also the impedance spectrums and their change due to the depletion show similar phenomenon. The resistance R_1 seems to be influenced by the depletion in some degree. The increase of this component is undoubtedly caused by the depletion of the electrolyte. Much larger effect is observed on the remaining components. The change of resistance R_2 is very high for the gel containing cadmium salt only. If some part of Cd ions is replaced by lithium cations, this effect almost vanishes. The same is apparent for the component Q . It is high for gels containing 70%

of cadmium, similarly to the voltammograms. The small amount of inert lithium ions lowered the effect of depletion and the component Q (having the nature of an admittance) is rather high. Also an interesting effect was observed on the diffusion component W, which decreased strongly by the depletion of gels with the highest Cd fraction. This way, the detrimental effect of transference numbers on metal electrodeposition from gels was clearly demonstrated.

CONCLUSION

Apparently, the depletion of gel on electroactive species seems unpleasant and may cause difficulties in lithium gel batteries. Further, the electrodeposition of cadmium can be used for modelling processes in lithium cells and other phenomenons by using cadmium instead of much more reactive lithium [10]. For the design of secondary lithium batteries containing, several advices can be drawn from the similarity between electrodeposition of cadmium and charging of lithium negative electrode (the electrodeposition of lithium). 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. Another possibility is offered by the use of a polymer possessing anionic functional groups [19] in a fashion similar to anion exchanging resins suitable for aqueous solutions. Also the improvement of Li ion transport by the presence of finely divided or even nanoparticle sized inert inorganic compounds such as silica [8], clay minerals [20] or alumina has been announced and would be worth of some reinvestigations. The results of such investigation will be published soon.

This drawback of a binary electrolyte was suppressed by the addition of lithium ions, which are electrochemically inactive in the potential range of cadmium electrodeposition. Unfortunately, it is hardly possible to find any cation which does not undergo electrochemical reaction at potential more negative than the potential of lithium electrode, and this method does not seem applicable for lithium batteries. Perhaps the use of organic, sufficiently stable cations (tetraalkylammonium salts or others) should be tested for that purpose.

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