

Study on poly(ethylene-oxide) electrolytes with ionophores for lithium batteries

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Abstract

Kinetics and mechanism for the electrodeposition of lithium from tetraethylene glycol dimethyl ether electrolytes formed from lithium perchlorate and ionophores have been studied using voltammetric and chronoamperometric methods at Pt and Au electrodes. The ionophore influence on stripping efficiencies, nucleation overpotentials, exchange current densities was evaluated. The type of nucleation and crystal growth process was determined. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The idea to use lithium complexing ligands (such as cyclic ethers or cryptands) with a purpose to improve ionic transport in polyether-based electrolytes comes from the research on lithium batteries systems [1–3]. It is generally expected that crown ethers or podands matching the size of Li^+ can segregate anion from cation. Thus, those ionophores added to electrolyte may prevent formation of ion pairs.

The aim of our work was to find out the influence of selected ionophores on lithium plating and stripping process from liquid electrolytes based on linear polyether.

The studied electrolytes contained LiClO_4 in tetraethylene glycol dimethyl ether and different lithium complexing agents. Crown ethers; 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), dibenzo-18-crown-6 (DB18C6), (the last one excluded from further studies as non soluble), and podand: [*N,N,N',N',N'',N''*-hexacyclohexyl-4,4'4''-propylideno-tris (3-oxabutyramide)] ($\text{C}_{48}\text{H}_{83}\text{N}_3\text{O}_6$ Ionophore VIII) have been tested.

The ratio of Li^+ /ionophore in the examined solutions was 10:1. The Ionophore VIII and crown ether 15C5 improved conductivity of the electrolyte, solid (B15C5) and liquid 12C4 added to LiClO_4 in tetraglyme electrolyte have negligible influence on electrolyte conductivity. The above mentioned ligands have different coordination num-

ber. Four is a coordination number for 12C4. Crowns 15C5 and B15C5 coordinate using five ether oxygen atoms [4]. Ionophore VIII is known as hexa-coordinated lithium ligand with three carbonyl centres and also three ether coordinating oxygen atoms. It has been tested as a successful medium for lithium selective electrodes. The crystallographic structure of ionophore VIII suggests that it may effectively segregate cation from anion in electrolytes [5,6].

2. Experimental

Tetraethylene glycol dimethylether ($\text{CH}_3\text{O}(\text{CH}_2-\text{CH}_2\text{O})_4\text{CH}_3$ 'tetraglyme', (Aldrich Chemical, Gold Label) was dried over molecular sieves (4 Å). Liquid crown ethers 12C4 and 15C5 (Aldrich Chemical 98%) were also dried over molecular sieves. Solid crown ether B15C5 (Fluka Chemicals) was dried under vacuum at 60°C for 24 h. The lithium ionophore VIII was designed, synthesized and made kindly available by Bocheńska [4] and was used as received.

The lithium perchlorate (Aldrich Chemical) was dried under vacuum approximately for 48 h at 120°C. The liquid electrolytes were prepared by dissolution of a lithium complexing agent in the solution containing LiClO_4 . The solution concentrations were all about 0.2 M with respect to LiClO_4 and 10 times lower considering added lithium ligand (L). The electrolytes were prepared using an ultrasonic bath.

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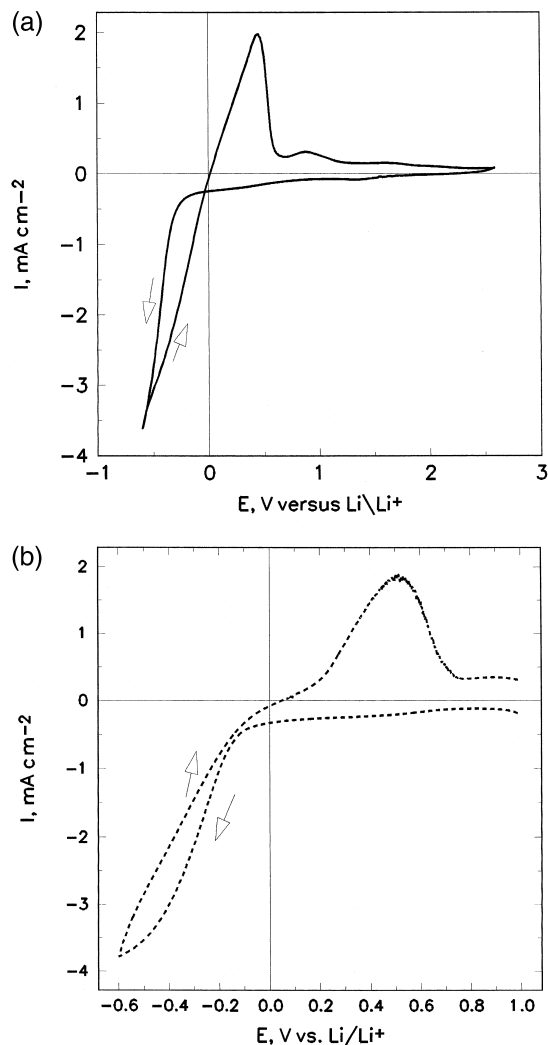


Fig. 1. Cyclic voltammograms of lithium plating and stripping at a 0.5 mm diameter platinum electrode vs. Li/Li^+ in tetraglyme containing: (a) LiClO_4 (0.188 M); (b) LiClO_4 (0.195 M) and Ionophore VIII (0.015 M).

The experiments were carried out in a home-made box filled with argon.

The electrochemical measurements were carried out in two-electrode, one compartment cell. A gold electrode (100 μm diameter) and platinum electrode (0.5 mm diame-

ter) served as working electrodes. A lithium metal wire (Aldrich Chemical) was used as a counter-reference electrode.

Cyclic voltammetry and chronoamperometry measurements were performed using an AutoLab system model PGSTAT10 potentiostat Eco-Chemi (The Netherlands) controlled with an IBM compatible PC.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry was used to get information on an ionophore influence on a kinetics and mechanism of a lithium deposition and a dissolution process.

Fig. 1 shows voltammograms run at sweep rate of 10 mV s^{-1} at a 0.5 mm Pt electrode in tetraglyme containing (a) only ca. 0.2 M LiClO_4 and (b) 0.2 M LiClO_4 and ca. 0.02 M Ionophore VIII. Both curves present similar shape indicating that a lithium deposition is being preceded by other electrochemical reactions. One of those processes takes place at Pt electrode at the potential +1.5 V vs. Li/Li^+ . This process was earlier found by Sylla et al. at a stainless steel electrode [7] and by Christie et al. [8] at a Ni microelectrode in polyether electrolytes. Sylla et al. [7] suggests that reduction of impurities is responsible for the observed cathodic current or that the observed process is a feature of the lithium salt [8]. The present measurements being taken on a different electrode substrate would rather point at the second explanation, but without further studies of the electrode surface, there is no unequivocal answer. The second, reversible growth of cathodic current density is recorded at $E = +0.6 \text{ V vs. Li}/\text{Li}^+$, presumably responding to the formation of Pt/Li alloy [9]. The surface of the electrode was not examined.

The main electrode process, lithium plating and stripping is clearly expressed by a rapid growth of a cathodic current density and a sharp anodic peak responding to an electro-dissolution of metal. A small hump following an anodic peak responds to the removal of lithium from the Li–Pt alloy formed earlier.

Table 1

Some electrochemical parameters obtained at a $1.96 \times 10^{-3} \text{ cm}^2$ disc Pt electrode vs. Li/Li^+ by cyclic voltammetry; sweep rate $\nu = 10 \text{ mV s}^{-1}$, $T = 298 \text{ K}$

Electrolyte Ligand (M)	LiClO_4 (M)	Nucleation overpotential, η (V)	Anodic peak potential, E_{pa} (V)	E_{hump} (V)	Limited cathodic current density, I_{L} (mA cm^{-2})	Cathodic current density at $\eta = -0.35$, I (mA cm^{-2})		Stripping efficiency, w_i (%)
						Forward scan	Reverse scan	
–	0.188	–0.180	0.50	0.80	4.52	1.82	2.61	62
Ionophore VIII 0.015	0.195	–0.125	0.60	–	3.80	2.20	1.50	40
B15C5 0.019	0.190	–0.150	0.50	0.75	4.50	1.80	2.45	45
15C5 0.019	0.188	–0.140	0.40	–	> 1.80	1.14	0.68	20
12C4 0.018	0.188	–0.080	0.40	0.80	3.35	2.28	1.50	< 20

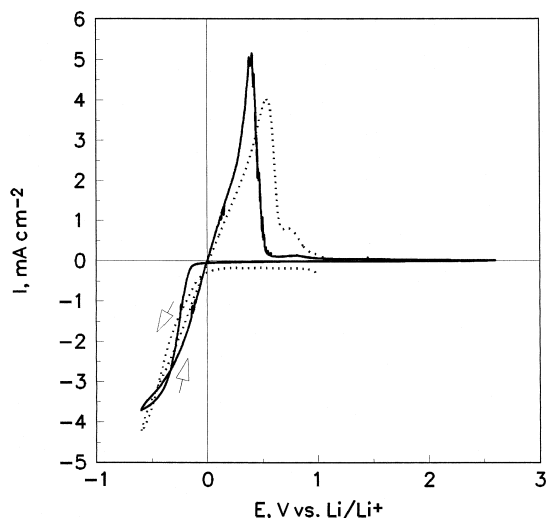


Fig. 2. Cyclic voltammograms of lithium plating and stripping in tetraglyme with 0.19 M LiClO_4 and 0.019 M B15C5 at a 100 μm diameter Au electrode vs. Li/Li^+ (—) and at a 0.5 mm diameter Pt electrode vs. Li/Li^+ (· · ·).

The characteristic parameters for a lithium deposition and dissolution process at a Pt electrode are shown in Table 1. As can be seen, the stripping efficiencies are lower than those found by Christie et al. for tetraglyme electrolytes measured at Ni electrode in higher concentrated electrolytes [8]. Liquid crown ethers such as 15C5 and 12C4 cause significant decrease in cathodic current efficiency down to 20%. Such influence was not observed in earlier work by Nagasubramanian et al. presenting effects of crown ether 12C4 on electrochemical performance of cathodes in polymer electrolytes [10].

Nucleation overpotentials (η) depend on the type of added ligand. The electrolyte containing liquid crown 12C4 shows the lowest value for η equals to -0.08 V vs. Li/Li^+ . Taking into consideration that the only 10% of Li^+ cations may form complexes with added ligand, measured effect seems to be strong. Other lithium ionophores exhibit less pronounced influence, however all of them cause decrease of the nucleation overpotential.

Cathodic current densities measured at the same overpotential at the forward and reverse scan may be an apparent measure of a growth of an electrode active surface area.

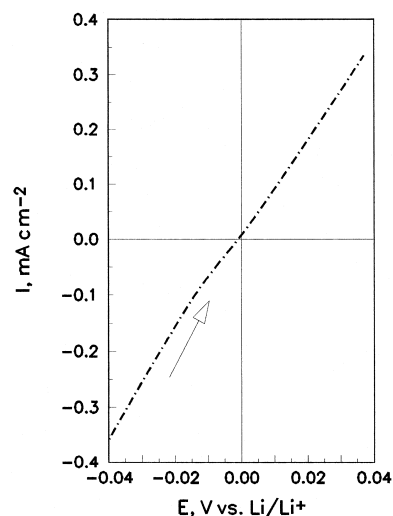


Fig. 3. Reverse sweep of voltammogram for LiClO_4 (0.19 M) and B15C5 (0.019 M) in tetraglyme at a 100 μm Au electrode vs. Li/Li^+ , sweep rate 10 mV s^{-1} .

Electrolytes containing Ionophore VIII, 15C5 and 12C4 ligands show lower current densities on a reverse scan. Only electrolyte containing crown ether B15C5 shows hysteresis on a voltammogram as electrolyte without added ionophores.

Anodic current peaks recorded for the Li dissolution from LiClO_4 with 12C4, 15C5 and Ionophore VIII electrolytes are broader than peaks illustrating stripping process from (i) LiClO_4 and (ii) LiClO_4 with B15C5 electrolytes. The broad stripping peaks indicate that the dissolved deposit is not uniform [11]. One may suppose that passivating layers formed on freshly deposited metal are not of the same type (known as Solid Electrolyte Interface [12]) in all cases. Also no evidence of a decomposition of added ionophores was recorded on cv-curves, it is likely that additives 15C5 and 12C4 take part in chemical reaction following lithium deposition causing modification of a surface. Further surface investigation are necessary to prove the above assumption.

Table 1 presents limited current values (I_L). The lowest I_L value was measured for electrolyte containing crown 15C5. Presumably I_L responds not only to electrolyte

Table 2

Some electrochemical parameters obtained at a 100 μm Au microelectrode vs. Li/Li^+ by cyclic voltammetry; sweep rate $v = 10 \text{ mV s}^{-1}$, $T = 298 \text{ K}$

Electrolyte	Nucleation overpotential, η (V)	Anodic peak potential, E_{pa} (V)	E_{hump} (V)	Exchange current density, I_o (mA cm^{-2})	αn_c	αn_a	Stripping efficiency, w_i (%)
Ligand (M)	LiClO_4 (M)						
—	0.188	-0.20	0.49	1.0	0.36	0.56	42
Ionophore VIII 0.015	0.195	-0.15	0.48	1.0	0.12	0.40	35
B15C5 0.019	0.190	-0.18	0.49	—	0.40	0.58	45
15C5 0.019	0.188	-0.15	0.42	0.8	0.20	—	< 20
12C4 0.018	0.188	-0.12	0.50	0.8	0.24	0.42	< 25

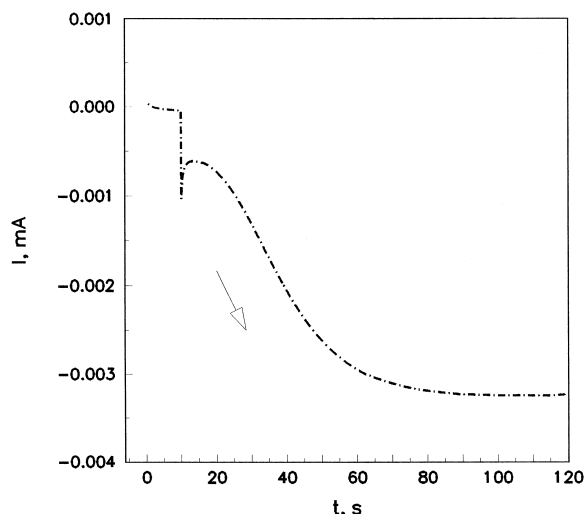


Fig. 4. Chronoamperometric curve of the nucleation and growth of lithium obtained from the electrolyte containing 0.195 M LiClO_4 , and 0.015 M Ionophore VIII in tetraglyme at a 0.5 mm Pt electrode vs. Li/Li^+ . Step potential $\eta = -0.35$ V.

transport properties, but illustrates also the state of the electrode surface in this case. Other ligands except B15C5 cause minor decrease in cathodic current densities.

To obtain exchange current densities and measured values of transfer coefficients, all studied ligands have been tested at a gold microelectrode. Fig. 2 shows voltammogram obtained at the Au electrode taken at a sweep rate of 10 mV s^{-1} in tetraglyme containing ca. 0.2 M LiClO_4 and ca. 0.02 M B15C5. The dotted line shows a voltammogram obtained at a Pt electrode from the same electrolyte. The contribution of prewaves on Au electrode is only noticeable at the $E = +0.8$ V vs. Li/Li^+ . According to Aurbach and Granot, Li UPD on gold peaks appear around +0.6 (cathodic) and 1.1 V stripping in electrolyte solutions based on 'glyme' solvents [13].

Some characteristic data on the lithium deposition–dissolution process at an Au microelectrode are shown in Table 2. Apparent values of transfer coefficients were calculated from a backward part of the cv curve.

Fig. 3 shows the part of a typical reverse scan at low overpotentials used for the calculation of the exchange

current density, (I_0), from the linear part of the voltammogram using expression:

$$I_0 = RT/nF \left(\frac{\partial I}{\partial \eta} \right)_{\eta \rightarrow 0}$$

where all symbols have their usual meaning.

Exchange current densities are all of the same range, the highest values are found for LiClO_4 and LiClO_4 with B12C4 electrolytes. The lowest values of I_0 are noticed for ionophore VIII and liquid crown ethers 12C4 and 15C5. The transfer coefficients αn_c and αn_a lies between 0.56 to 0.35 indicating that one-electron process is not affected by the passive layer formation at its very early stage [14].

Studied ligands cause decrease of the nucleation overpotentials, showing that ionophores are easier removed from the cation coordination shell than polyether molecules.

From the data gathered in Tables 1 and 2, it can be seen that lithium ionophores affect the studied deposition–dissolution processes in a similar way on both electrode substrates (Pt, Au), slowing the rate of electrode reaction and causing decrease in the nucleation overpotential.

3.2. Chronoamperometry

Chronoamperometry was used for the determination of the nucleation type and a crystal growth of the lithium phase. Measurements were taken on the Pt macroelectrode and the Au microelectrode. With the purpose to avoid an UPD or alloy formation influence on chronoamperometric measurements, both electrodes were kept at the $E = 0.5$ V vs. Li/Li^+ for 10 s before the cathodic overpotential was applied. Fig. 4 shows a typical current transient obtained in tetraglyme containing ~ 0.2 M LiClO_4 and 0.015 M of Ionophore VIII at a Pt electrode. The slope of the rising part of a cathodic curve expressed in a logarithmic scale $\Delta \log I / \Delta \log t$ is closed to 0.5—the value corresponding for the three dimensional (3D) nuclei growth under kinetic control [15]. Table 3 presents the results obtained from the current transient at a Pt and Au electrodes reflecting differences in morphology of the deposit at its early stage of formation from tetraglyme electrolytes containing ionophores. As was explained by Christie and Vincent [16], more reliable analysis of chronoamperometric curves

Table 3

Type of nucleation and crystal growth obtained at a $1.96 \times 10^{-3} \text{ cm}^2$ Pt electrode vs. Li/Li^+

Electrolyte		$\Delta \log I / \Delta \log t$	Type of crystal growth	Nucleation type	r^2
Ligand (M)	LiClO_4 (M)				
–	0.188	0.35/0.65*	3D nuclei kinetic control	instantaneous	0.999
Ionophore VIII 0.015	0.195	0.66/0.50*	3D nuclei kinetic control	instantaneous	0.998
B15C5 0.019	0.190	0.58/1.5*	3D nuclei kinetic control	instantaneous/progressive*	0.998/0.998
15C5 0.019	0.188	0.33	3D nuclei kinetic control	instantaneous	0.999
12C4 0.018	0.188	0.38	3D nuclei diffusion control	instantaneous	0.999

*At a 100 μm Au microelectrode.

providing information of nucleation and crystal growth should involve non-linear least-squares fits to prolonged current-transient expressions. Our results based on a simple linear fit of rising section to appropriate function of t , when nuclei overlap does not occur should be treated as a first approximation. The results seem to be satisfactory as prolonged current-transient in low concentrated electrolytes (0.2 M) is likely to be influenced by the following film formation process. However, to reduce all ambiguities in determination of the surface morphology further microscopic studies are required.

4. Conclusion

Our preliminary results on the influence of ionophores on the deposition and electrodisolution of lithium from linear ether based electrolytes show possibility of practical application of chosen complexing ligands.

Acknowledgements

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