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Conductivity and interfacial behaviour of bis-1,4-dioxapentyl sulfate (IV) and 1,4,7-trioxaoctyl sulfate (IV) based electrolyte for lithium batteries

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Abstract The electrolytic conductivity and viscosity of lithium perchlorate in bis-1,4-dioxapentyl sulfate (IV) [OS22] and 1,4,7-trioxaoctyl sulfate (IV) [OS32] were determined as a function of salt concentration (0.00005– 2 M) and temperature (286–318 K). At 298 K, the highest conductivity ($\kappa = 2.77 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$) was achieved for OS22 based solutions containing 1-2 M LiClO₄. Formation of electrically neutral ion pairs appeared to be the main reason for a continuous decline in the molar conductivity (Λ) observed in dilute solutions with increasing salt concentration. Additionally, an increase in the dynamic viscosity (n) accounted for a decrease in the mobility of charge carriers with increasing length of the oxaalkyl chain in the podand molecules. The temperature dependence of the conductivity and viscosity was found to be of the Arrhenius type for both systems investigated, while the activation energies, $E_{\kappa}^{\ \#}$ and $E_n^{\#}$, varied in parallel with the degree of interionic aggregation. CVs obtained on a polycrystalline Pt electrode indicated the electrochemical stability of OS22 in the potential range between -0.8 V and 4.7 V versus Li^+/Li . A linear current density-potential dependence, with the same slope for the anodic and cathodic branches proved the reversibility of lithium electrodeposition and re-dissolution at the Pt/1 M LiClO₄ + OS22 interface.

Keywords Oxaalkyl podand solvents · Conductivity · Viscosity · Lithium electrodeposition–dissolution · Platinum electrode

Introduction

Bis-oxaalkyl sulfates (IV), a novel group of recently synthesised podand compounds [1] have been recognised as effective complexing agents for alkali metal and alkali earth metal cations. Our previous spectroscopic investigations [2] revealed that Li⁺ cations are almost quantitatively coordinated to the ether oxygens of bis-1,4-dioxapentyl sulfate (IV) [OS22] and/or 1,4,7-trioxaoctyl sulfate (IV) [OS32], producing 1:1 complexes. The ¹³C- and ⁷Li NMR spectra provided evidence for a fast fluctuation of Li⁺ cations between all the oxygen atoms in an open ring-like channels formed by the oxaalkyl chains of podand molecules studied.

The above mentioned features along with a chemical stability and fire resistance have stimulated our interest in the bulk and interfacial electrochemical behaviour of bis-oxaalkyl sulfates (IV). Recently, upon development of lithium batteries it has been found that solubility and dissociation of lithium salts in aprotic low-molecular and polymeric solvents, as well as consequently the conductivity level of the resulting electrolyte systems, may be enhanced by introducing various oxo- and aza(oxo)-ligands, such as crown ethers, cryptands or calixarenes [3 and refs. therein, 4, 5, 6]. Up to now, however, the relevant data for podands have been very scarce [7, 8, 9]. This paper reports results of a study of the effect of salt concentration, temperature and the oxaalkyl chain length on the conductivity and viscosity of the OS22 and OS32 based LiClO₄ solutions. Furthermore, the resistance of OS22 based electrolyte against electrooxidation at high positive potentials and the kinetics of lithium deposition-dissolution is characterized by cyclic voltammetry.

Experimental

Bis-1,4-dioxapentyl sulfate (IV) and 1,4,7-trioxaoctyl sulfate (IV) were synthesised and purified according to the procedures given in the previous work [1]. According to the Karl Fischer titration, the

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water content of the purified solvents was less than 0.01%. LiClO₄ was re-crystallised twice from water and dried at 393 K in a vacuum oven prior to use. All electrolyte preparations as well as transfer of solvents and solutions into the experimental cells were performed in an inert atmosphere dry box.

The resistance of solvents and electrolyte solutions was measured in a glass cell with two slightly platinized Pt electrodes, using a precise a.c. conductance bridge with a sinusoidal generator GFT 73 ZDZ-Warsaw (3–10 kHz). The cell constant was repeatedly determined prior to each series of measurements using KCl aqueous solutions of known conductivity. The relative permittivity (ϵ) of the solvents was determined with the use of an impedance analyser Solatron 1260 (3–100 kHz). Ubbelohde viscometers were used to determine the dynamic viscosity coefficients (η). The relative η values were determined in comparison with the standard value of 0.8937 cP for H₂O and 2.513 cP for PC at 298 K [10]. The density of solvents and solutions (d) was measured with a pycnometer. The temperature of the systems under investigation was controlled at ± 0.01 K.

The voltammetric behaviour of the OS22 based 1 M LiClO₄ solution was tested in a one compartment glass cell with a polycrystalline Pt sheet of 0.85 cm² geometric area as a working electrode and a Pt wire of ~10 cm² geometric area as a counter electrode. A reference Li⁺/Li electrode in the same electrolyte solution was equipped with Luggin capillary [11]. A standard voltammetric apparatus consisted of a potentiostat (Elpan EP20), a wave generator (Elpan EG20) and a *X*, *Y* recorder (endim 620.02). The pre-treatment procedure included activation of the working electrode in 0.5 M H₂SO₄ by cycling (1 V s⁻¹) between 0.05 V and 1.5 V until a stationary voltammogram was obtained. Next, the roughness factor of Pt (rf=3.5) was determined from the charge corresponding to the reductive adsorption and/or oxidative desorption of hydrogen, assuming that a hydrogen monolayer requires 0.210 mC cm⁻² [12].

Results and discussion

Conductivity and viscosity

Figure 1 shows the concentration dependence of the conductivity (κ) of LiClO₄ solutions in OS22 $(d=1.143 \text{ g cm}^{-3})$ $(d=1.143 \text{ g cm}^{-3}, \epsilon=20.1 \text{ at } 298 \text{ K})$ and OS32 $(d=1.171 \text{ g cm}^{-3}, \epsilon=19.4 \text{ at } 298 \text{ K})$. Starting from the $LiClO_4$ concentration (c) of 0.00005 M, an increase in the amount of ionic carriers results in the conductivity increase in both systems investigated. Then the value of κ of OS22 based solutions achieves a maximum at about 1 M LiClO₄ and remains constant up to \sim 2.5 M at the level of $2.77 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$. When OS32 is used as the solvent, it decreases from the maximum value of $1.46 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ with the LiClO₄ concentration increasing above 1.5 M. The data in Fig. 1 demonstrate that the conductivity of the OS22 is about two times higher than that of the OS32 based solutions over the whole concentration range investigated.

As evidenced in Fig. 2, the molar conductivity (Λ) of both OS22 and OS32 based electrolyte continuously decreases with increasing amount of LiClO₄. For dilute solutions ($c \le 3.2 \times 10^{-7} \epsilon^3$ M at 298 K [13], where ϵ denotes the relative permittivity of the solvent) the plot of the experimental Λ values versus the square root of the salt concentration is linear, with the slope greater than expected on the basis of the Onsager equation for completely dissociated electrolytes [14]. This behaviour



Fig. 1 Conductivity as a function of LiClO₄ concentration in (1) bis-1,4-dioxapentyl sulfate (IV) [OS22] and (2) 1,4,7-trioxaoctyl sulfate (IV) [OS32]; T = 298 K



Fig. 2 Molar conductivity as a function of the square root of LiClO₄ concentration in (1) bis-1,4-dioxapentyl sulfate (IV) [OS22] and (2) 1,4,7-trioxaoctyl sulfate (IV) [OS32], T = 298 K

can be rationalised in terms of a successive formation of uncharged ion pairs and thus a suppression in the number of ionic carriers with increasing salt concentration because of increasingly stronger mutual interactions between ClO_4^- anions and Li^+ cations accommodated in channels between the oxaalkyl chains of the podand molecules (P).

Upon assumption that the Li^+ cations coordinated to the ether oxygens within the oxaalkyl chains exist in equilibrium with uncomplexed Li^+ cations and neutral interionic clusters:

$$\mathrm{Li}^{+} + \mathrm{P} + \mathrm{ClO}_{4}^{-} \stackrel{K_{a}}{\rightleftharpoons} \left(\mathrm{Li}^{+} \mathrm{P}\right) + \mathrm{ClO}_{4}^{-} \stackrel{K_{a}}{\rightleftharpoons} \left(\mathrm{Li}^{+} \mathrm{P} \, \mathrm{ClO}_{4}^{-}\right) \qquad (1)$$

the experimental equilibrium constant (*K*) between the uncharged and ionic species is related to the formation constant of the complex between Li⁺ cations and solvent molecules (K_f) and to ion pairs association constant (K_a) according to the expression: $K = K_a \{1/[1 + (1/K_f c_S)]\}$. The symbol c_S denotes the concentration of the complexing agent. Because for the systems investigated $(1/(K_f c_S) \leq 1 \ [15]$ and thus $K \approx K_a$, analysis of the experimental data based on the Fuoss–Krauss equation:

$$F(z)/\Lambda = 1/\Lambda_{\rm o} + c\Lambda f_{\pm}^2 K_{\rm a} / \left[\Lambda_{\rm o}^2 F(z)\right]$$
⁽²⁾

and the tabulated F(z) function values [13] permits evaluation of the ion pairs association constant K_a along with the limiting molar conductivity Λ_o . The corresponding linear plots are depicted in Fig. 3. Using the numerical method, upon assumption of 1 M as a standard concentration, we obtained $K_a = 256 \pm 3$ and $\Lambda_o = 28.5 \pm 0.1 \ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for the LiClO₄/OS22 system, while $K_a = 2270 \pm 30$ and $\Lambda_o = 19.5 \pm 0.1 \ \Omega^{-1}$ cm² mol⁻¹ was calculated for the LiClO₄/OS32 system.

According to the K_a values determined, the relative fraction of ClO_4^- anions interacting with the complexed Li^+ cations strongly enough to promote a formation of ion pairs, appears to be considerably higher in OS32 than in OS22 solutions. The reason might be a weaker repulsive interaction between ClO_4^- anions and the sulfate group of the podand molecule with Li^+ cations coordinated to the ether oxygen sites in 4 and 7 positions than in 1 and 4 positions. Therefore, the counter-ions would be liable to come near the Li^+ cations in OS32 based solutions.

Since the ϵ value was proved to be almost the same for both solvents, it is plausible that the difference in mobilities of charge carriers, and consequently in κ and Λ , is mainly caused by an increase in the solvent viscosity with increasing length of the oxaalkyl chain in the podand molecules. This conclusion is supported by the fact that the conductivity ratio of the OS22 and OS32 based solutions (see Fig. 1) corresponds well to the viscosity ratio. At 298 K, the coefficient of dynamic viscosity (η) was found to be equal 2.05 cP and 5.09 cP for pure OS22 and OS32, respectively. Additionally, a lower conductivity of LiClO₄ + OS32 solutions than that of the LiClO₄ + OS22 solutions may be also connected with a larger effective radius of the solvated Li⁺ cation in the former system.

It is worth noting that up to the LiClO₄ concentration of 0.05 M, the corrections for viscosity changes in the OS22 and OS32 based solutions can be neglected. However, specific interionic interactions of higher order than pairwise become appreciable for more concentrated electrolyte solutions, which is manifested as a continuous rise in the η value. For the LiClO₄ + OS22 system at 298 K we have found $\eta = 2.90$ cP, 4.52 cP and 6.48 cP at salt concentrations of 0.5 M, 1 M and 1.5 M, respectively. Measurements for 1 M LiClO₄ + OS32 solution revealed $\eta = 16.49$ cP.

An increase in dissociation degree of ion multiplets should be expected with increasing temperature. In fact, the viscosity of solutions decreases with increasing temperature, while the opposite effect is observed for the conductivity. As shown in Figs. 4 and 5, changes in the conductivity and viscosity of the solutions studied over the temperature range 286–318 K satisfy the Arrhenius equation. The corresponding activation energies are listed in Table 1. It is characteristic that an increase in the degree of interionic aggregation with increasing salt concentration and/or replacement of OS22 solvent with OS32 results in higher activation energy of both conductivity and viscosity. One can state that independently of the length of the oxaalkyl chains in the podand molecules, the activation energies obtained from the viscosity data $(E_{\eta}^{\#})$ at fixed salt concentration are by about 20 kJ mol⁻¹ higher than those calculated from





Fig. 3 Plots of $F(z)/\Lambda$ versus $[c\Lambda f_{\pm}^2/F(z)]$ for diluted LiClO₄ solutions in (1) bis-1,4-dioxapentyl sulfate (IV) [OS22] and (2) 1,4,7-trioxaoctyl sulfate (IV) [OS32]

Fig. 4 Temperature dependence of the conductivity $(\kappa/\Omega^{-1} \text{ cm}^{-1})$ for solutions: (1) 0.05 M LiClO₄+OS22, (2) 1 M LiClO₄+OS32, (3) 1 M LiClO₄+OS22, (4) 1.5 M LiClO₄+OS22





Fig. 5 Temperature dependence of the coefficient of dynamic viscosity (η /Poise) for solutions (1) 0.05 M LiClO₄+OS22, (2) 1 M LiClO₄+OS22, (3) 1.5 M LiClO₄+OS22, (4) 1 M Li-ClO₄+OS32

the conductivity data $(E_{\kappa}^{\#})$. A similar effect was earlier observed in concentrated aqueous solutions of LiBr and NH₄Br [16]. Thus, it seems plausible that the viscous flow is determined mainly by the movement resistance of ion pairs and multiple ion aggregates, while the charge transport in the $LiClO_4 + OS22$ and $LiClO_4 + OS32$ systems occurs, at least in part, by hopping of individual Li⁺ cations between neighbouring solvent clusters. As follows from the A value obtained for OS22 based 1 M LiClO₄ solution, the sum of the cations and anions mobilities is equal to 25×10^{-6} cm² s⁻¹ V⁻¹. Consequently, assuming the potential difference of 3 V across a 0.3 cm thick layer of the solution between the electrodes, typical of lithium cells, the rate of charge transport should be of about 3 μ m s⁻¹. On the molecular scale it means that the Li^{+} cation passes about 10^4 solvent molecules per second. In view of the actual state of knowledge about the electrolytes indispensable for the lithium batteries [3,17, 18, 19, 20, 21, 22, 23, 24, 25, 26],

Table 1 Activation energies of conductivity $(E_{\kappa}^{\#})$ and viscosity $(E_{\eta}^{\#})$ for OS22 and OS32 based LiClO₄ solutions

Solution	$E_{\kappa}^{\#}$ (kJ mol ⁻¹)	$E_{\eta}^{\#}$ (kJ mol ⁻¹)
0.05 M LiClO ₄ in OS22 1 M LiClO ₄ in OS22 1.5 M LiClO ₄ in OS22 1 M LiClO ₄ in OS32	$\begin{array}{c} 9.9 \pm 0.4 \\ 15.4 \pm 0.9 \\ 17.5 \pm 0.7 \\ 22.3 \pm 0.4 \end{array}$	$\begin{array}{c} 28.6 \pm \ 0.9 \\ 33.8 \pm 0.4 \\ 36.0 \pm 0.9 \\ 43.6 \pm 0.3 \end{array}$

some improvement in the conductivity can be expected by reducing the viscosity and/or the degree of electrolyte association through a combination of OS22 or OS32 with appropriate organic co-solvents and/or lithium salts.

Voltammetric characteristics

Not only the conductivity but also the electrolyte stability is of primary importance for the long life charge and discharge performance of the secondary batteries [3,17,18, 27, 28, 29]. Information on the electrochemical reactivity of the OS22 based 1 M LiClO₄ solution was obtained in a series of potentiodynamic experiments at a polycrystalline Pt electrode. As expected, the representative CVs in Fig. 6 indicate an excellent cyclability of the system over a wide potential window between -0.8 V and 4.7 V versus Li⁺/Li, without any reductive or oxidative decomposition of OS22. The lithium electrodeposition and re-dissolution, both starting close to E=0 V versus Li⁺/Li, appear to be the only processes giving rise to the cathodic and anodic current, respectively, in the corresponding potential ranges: -0.8 V to 0 V and 0 V to 0.8 V. The fact that the charge related to the lithium dissolution is almost equal to that of the lithium deposition proves an excellent stability of OS22 against any electroreduction. Further, after removal of lithium from the Pt surface, being reflected in CVs as the anodic current peak with the maximum at about 0.6 V, there is no other evidence for any charge transfer up to the onset of a Pt surface oxidation, manifested by a small anodic current at E = 4 - 4.7 V. Taking into account the corresponding charge densities, there is no doubt that the cathodic current peak around 2.55 V upon the following negative sweep corresponds exclu-



Fig. 6 Cyclic voltammograms of a polycrystalline Pt electrode in 1 M LiClO₄+OS22 with the anodic potential limit of 5.2 V. Inset: lithium deposition and dissolution upon cycling between -0.8 V and 0.4 V; ν =0.01 V s⁻¹; T=298 K

sively to the electroreduction of a Pt oxide layer. This conclusion is supported by the observation that such a cathodic peak was absent in CVs when the anodic potential limit was restricted to $E \approx 3$ V. A progressive growth of the anodic current, due to an irreversible OS22 electrooxidation, is found only at the electrode potentials higher than 4.7 V.

Note that, in contrast to OS22, the reductive decomposition of the solvents actually often used in practical lithium batteries, such as ethylene carbonate (EC) and dimethyl carbonate (DMC), occurs on a graphite electrode with ethylene evolution already at E < 0.8 V [30, 31]. Various hydrocarbons (CH₄, C₂H₆, C_3H_6 and C_3H_8) are generated, along with a surface layer containing lithium alkyl carbonates, lithium alkoxy species and/or insoluble lithium salts, from the mixed solvents: propylene carbonate (PC), ethylmethvlcarbonate (EMC) and diethyl carbonate (DEC) [32, 33, 34]. On the other hand, these compounds do not undergo electrooxidation up to comparable or even somewhat higher positive potentials than OS22 [17, 18, 21, 22, 27, 35, 36, 37] depending on the electrode material.

It should be emphasised that the lithium electrodeposition and re-dissolution at the Pt/1 M LiClO₄ + OS22 interface occurs reversibly under potentiodynamic condition. This is clearly evidenced by the linear current density (*j*) versus potential (E) relationship with the same slope of the anodic and cathodic branches in successive cycles (see CVs in Fig. 6 and inset to Fig. 6) independently of the sweep rate (up to 100 mV s^{-1}). A similar, purely resistance behaviour, within the potential range much greater then that predicted by the Volmer–Butler equation, has been also reported for the Li⁺/Li electrode in SOCl₂ [38] and PC [34, 39]. The reason for such behaviour can be a super-imposition of the deposition/ dissolution of lithium with the formation/dissolution of a superficial surface layer that may be composed of both inorganic and organic compounds, including polymeric molecules.

In earlier works on the charge-discharge performance of Li in electrolytes with alkyl carbonates and ethers, it has been shown by the electrochemical and spectroscopic techniques that a surface layer with protective properties is formed on the metal surface instantly upon contacting the solution as well as later by the electroreductive decomposition of the solvent and/or the anion of the electrolyte [33, 34, 40, 41, 42 and refs. therein]. Evidence has been given that the chemical nature of the surface layer, dependent on the electrolyte composition, strongly affects the cyclability of Li electrodes, which was manifested among others by changes in their characteristic upon cycling in opposite directions [33, 34, 42]. In contrast, in our studies of the Pt/Li system in 1 M LiClO₄+OS22 solution we have not observed any hysteresis of the j-E curves recorded during the negative and positive sweep (Fig. 6). This fact together with a relatively low value of the reaction resistance obtained from the *j*-*E* plot ($R_r = 65.3 \pm 0.4 \ \Omega \ cm^2$)

suggests that the surface layer at the Pt/Li electrode is highly conductive for Li⁺ cations. The corresponding exchange current density is equal to $j_0 = RT/FR_r = 0.393 \pm 0.003$ mA cm⁻². Further studies should clarify the chemical nature and morphology of the Pt/Li surface in the OS22 based electrolyte solutions as well as the cycling performance of this electrolyte with respect to the electrodes commonly used in practical lithium batteries.

Conclusions

As proved by the above discussed bulk and interfacial behaviour, bis-1,4-dioxapentyl sulfate (IV) appears to be a suitable electrolyte solvent or co-solvent for battery applications. This compound satisfies the requirements of a high solubility of LiClO₄ and ensures an almost constant conductivity of $2.77 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at a salt concentration of 1–2.5 M. While the lithium electrode-position and re-dissolution occur reversibly at the Pt/ electrolyte solution interface, OS22 itself is immune to any electrochemical reduction or oxidation in the potential range –0.8 V to 4.7 V versus Li⁺/Li.

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References

- 1. Gierczyk B, Łęska B (1999) J Incl Phenom 35:327
- Schroeder G, Gierczyk B, Łęska B, Wojciechowski G, Pankiewicz R, Brzezinski B, Bartl F (2002) J Mol Struct 607:9
- 3. Afanase'ev WN, Grechin AG (2002) Uspekhi Chimii 71:878
- 4. Iwahori T, Mitsuishi L, Shiraga S, Nakajima N, Momose H, Ozaki Y, Tanigichi S, Awata H, Ono T, Takeuchi K (2000) Electrochim Acta 45:1509
- 5. Wrigh PV (2002) MRS Bull 27:597
- McBreen J, Lee HS, Yang XQ, Sun X (2000) J Power Sources 89:163
- 7. Lisowska-Oleksiak A, Inerowicz HD (1999) J Power Sources 81–82:813
- Lisowska-Oleksiak A, Kazubowska K, Lis M (2000) Symposium of the Polish Supramolecular Chemistry Network, Olsztyn
- Morford RV, Kellam EC, Hofmann MA, Baldwin R, Allcock HR (2000) Solid State Ionics 133:171
- Saito Y, Yamamoto H, Nakamura O, Kageyama H, Ishikawa H, Miyoshi T, Matsuoka M (1999) J Power Sources 81–81:772
- Bełtowska-Brzezinska M (A. Mickiewicz University) (1991) PL Patent 151 145
- 12. Biegler T, Rand DAJ, Woods R (1971) J Electroanal Chem 29:269
- 13. Fuoss RM (1935) J Am Chem Soc 57:488
- 14. Onsager L (1926) Physik Z 27:388
- Schroeder G, Gierczyk B (2002) Zastosowanie magnetycznego rezonansu jądrowego w chemii supramolekularnej, In: Chemia supramolekularna. Betagraf, Poznań, p 30
- 16. Lo Surdo A, Wirth HE (1979) J Phys Chem 83:879
- 17. Tarascon JM, Guyomard D (1994) Solid State Ionics 69:293
- 18. Guyomard D, Tarascon JM (1995) J Power Sources 54:92

- 20. Abraham KM, Alamgir M (1993) J Power Sources 43-44:195
- 21. Herr R (1990) Electochim Acta 35:1257
- Dudley JT, Wilkinson DP, Thomas G, LeVae R, Woo S, Blom H, Horvath C, Juzkow MW, Denis B, Juric P, Aghakian P, Dahn JR (1991) J Power Sources 35:59
- 23. Cisak A, Werblan L (1986) Wysokoenergetyczne niewodne ogniwa galwaniczne. PWN, Warsaw
- 24. Tobishima S-I, Okada T (1985) Electrochim Acta 30:1715
- 25. Tobishima S-I, Arakawa M, Yamaki J-I (1988) Electrochim Acta 33:239
- 26. Matsuda Y, Morita M, Yamada K, Hirai K (1985) J Electrochem Soc 132:2538
- 27. Morita M, Yamada O, Ishikawa M (1999) J Power Sources 81–82:425
- Watanabe H, Nohma T, Nakane I, Yoshimura S, Nishio K, Saito T (1993) J Power Sources 43–44:217
- Takahashi M, Yoshimura S, Nakane I, Nishio K, Saito T, Fujimoto M, Narukawa S, Hara M, Furukawa N (1993) J Power Sources 43–44:253

- Joho F, Rykart B, Imhof R, Novak P, Spahr ME, Monnier A (1999) J Power Sources 81–82:243
- Novak P, Joho F, Imhof R, Panitz J.Ch, Haas O (1999) J Power Sources 81–82:212
- Kumai K, Miyashiro H, Kobayashi Yo, Takei K, Ishikawa R (1999) J Power Sources 81–82:715
- Aurbach D, Gofer Y, Ben-Zion M, Aped P (1992) J Electroanal Chem 339:451
- 34. Kanamura K, Tamura H, Takehara Z (1992) J Electroanal Chem 333:127
- Egashira M, Takahashi H, Okada S, Yamaki J (2001) J Power Sources 92:267
- 36. Kanamura K (1999) J Power Sources 81-82:123
- 37. Johnson BA, White RE (1998) J Power Sources 70:48
- 38. Peled E, Yamin H, (1979) Isr J Chem 18:131
- 39. Burrows B, Jasinski R (1968) J Electrochem Soc 115:365
- 40. Peled E (1979) J Electrochem Soc 126:2049
- 41. Peled E (1983) J Power Sources 9:253
- 42. Wiesener E, Eckoldt U, Rahner D (1989) Electrochim Acta 34:1277