

O.Yu. Egorkina · A.M. Skundin

The effect of temperature on lithium intercalation into carbon materials

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Abstract The effects of temperature on lithium intercalation into non-graphitized carbonized cloth from various electrolytes have been studied. The open-circuit potential (o.c.p.) of the intercalates shifts in the negative direction as the temperature is raised. The average temperature coefficient of the o.c.p. is equal to $-0.04 \text{ mV} \cdot \text{K}^{-1}$ in the range from -35 to $+45$ °C. Intercalation-deintercalation kinetics was studied by the galvanostatic technique. It was shown that this process is quasi-ohmic at room and higher temperatures and has activation-ohmic control at lower temperatures. The effective activation energy of intercalation-deintercalation is about $20 \text{ kJ} \cdot \text{mol}^{-1}$. Intercalates are corroded in all electrolytes, the corrosion rate being drastically increased as the temperature is raised. The apparent activation energy of corrosion is $120\text{--}150 \text{ kJ} \cdot \text{mol}^{-1}$. The corrosion rate is suggested to be controlled by cathodic reduction of electrolyte components.

Key words Lithium intercalation · Carbon electrodes · Temperature effects

Introduction

The process of lithium intercalation into carbonaceous materials is now the subject of numerous investigations following the success in the development of promising lithium-ion rechargeable cells with carbon negative electrodes. Meanwhile the question of temperature effects on the process is so far unresolved. Even the temperature coefficient of the reversible potential of lithium intercalates is unknown. The only exception is some work [1] in which the temperature dependence of the

open-circuit voltage for an Li/LiC_6 cell with a solid polymer electrolyte in the range from 76 to 117 °C is reported.

A comparison of the performances of commercial C-size cells from Sony Energetic at 22 and 37 °C is presented in [2]. Some temperature effects were found, including increase of capacity, increase of discharge voltage, decrease of internal resistance, and decrease of cycle life due to temperature increase. However, there was no attempt to investigate effects associated with the carbon negative electrode.

The object of the present work is to study the process of lithium intercalation into one kind of carbonaceous material, namely carbonized cloth, in the temperature range from -35 to $+45$ °C.

Experimental

Electrodes with a surface area of $1\text{--}1.5 \text{ cm}^2$ were made from non-graphitized carbonized cloth. X-ray diffraction studies showed that the carbonized cloth virtually did not contain a graphite phase. The interplanar distance $d(002)$ was 0.371 nm , and the average crystalline sizes along the c and a axes were 1.0 and 2.3 nm respectively. All measurements were carried out in Teflon or glass cells. The glass cells had water jackets. The Teflon cells were placed in a cryothermostat, while the glass cells were built into a circulation loop of the cryothermostat. Three non-aqueous electrolytes were studied: no. 1: 1 M LiClO_4 in propylene carbonate (PC), no. 2: 1 M LiClO_4 in a mixture of PC with dimethoxyethane (DME) (7:3), and no. 3: 1 M LiBF_4 in γ -butyrolactone. Counter-electrodes and reference electrodes were made from Li sheets. Cells were assembled and disassembled in an argon-filled glove box.

The open-circuit potential (o.c.p.) of the intercalate was found to be slowly shifted in the positive direction. This shift was associated with corrosion of the intercalate, i.e. with lithium depletion of the surface layer. Therefore, for estimation of the temperature coefficient of the o.c.p., the following technique was used. The cell was stored at room temperature (20 °C) and the o.c.p. drift was checked for ca. 1 h . Then the cell was placed in the cryothermostat at a pre-determined temperature and o.c.p. checking was continued. After removal of the cell from the cryothermostat the o.c.p. was checked for 30 min . An example of such an experiment is shown in Fig. 1. One can see that immediately after a temperature jump a potential peak is registered. This peak is associated with

O.Yu. Egorkina · A.M. Skundin (✉)
A.N. Frumkin Institute of Electrochemistry
of the Russian Academy of Sciences, 31 Leninsky Prospect,
117071 Moscow, Russia
Tel.: +7-095-955 4020; Fax: +7-095-952 0846

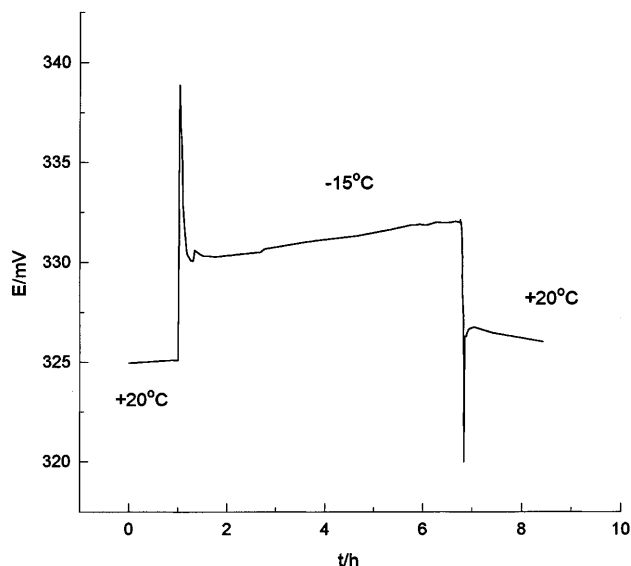


Fig. 1 An example of the o.c.p. recorded during temperature jumps in electrolyte no. 2

thermoelectrical effects due to uneven temperature distribution in this system, which has metallic and non-metallic components.

The kinetic measurements were made according to the procedure described in [2].

Results and discussion

Open circuit potential

Figure 2 shows the temperature dependence of the o.c.p. (E) for electrodes with the degree of intercalation (x in formula Li_xC_6) ca. 0.7. To avoid an uncertainty due to small differences x in various measurements, Fig. 2 shows not the potential values, but differences between

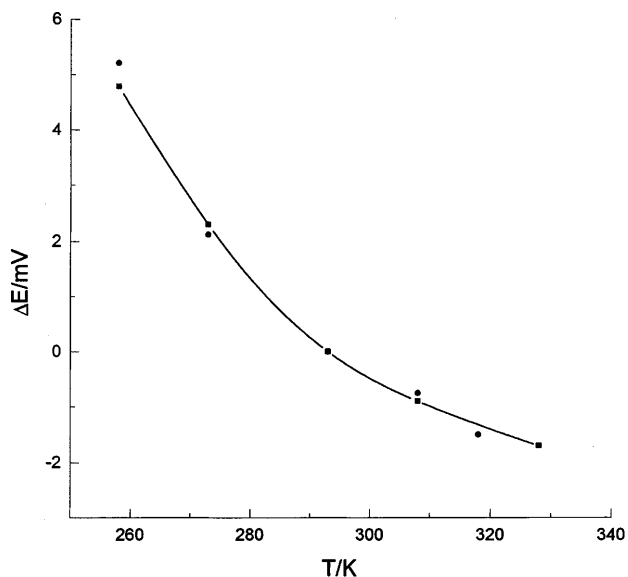


Fig. 2 Temperature dependence of the o.c.p. in electrolyte no. 2

the o.c.p. at given temperature and at 20 °C. Increase of temperature results in shift of the o.c.p. in the negative direction. The temperature coefficient of the o.c.p. changes from $-0.04 \text{ mV} \cdot \text{K}^{-1}$ at higher temperatures (35–45 °C) to $-0.20 \text{ mV} \cdot \text{K}^{-1}$ at temperatures below 0 °C. The average value of the temperature coefficient of the o.c.p. for the full range investigated is equal to $-0.12 \text{ mV} \cdot \text{K}^{-1}$. Therefore, the mean value of the entropy change (ΔS) for the intercalation reaction



calculated as $(\Delta S) = nF(\Delta E/\Delta T)$ is equal to $-12 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

The authors of [1] obtained a linear temperature dependence of the o.c.p. for intercalate LiC_6 , with a slope of $-0.0512 \text{ mV} \cdot \text{K}^{-1}$. This value coincides with figures obtained in the present work.

Intercalation-deintercalation kinetics

Figure 3 shows typical galvanostatic switch-on curves obtained in the first electrolyte (see Experimental section). In principle, almost the same curves were obtained in the other electrolytes studied. In all curves one can see a sharp potential jump and then a slow change. The potential jump is due to both IR drop and activation polarization; the slow change reveals growth of concentration polarization due to non-stationary diffusion. In principle, the curves of Fig. 3 are similar to switch-on curves for Li^+ intercalation into TiS_2 [3]. However, it must be noted that, in spite of the similarity of the cell geometry in the two cases, the initial potential jumps in the curves of Fig. 3 were an order of magnitude greater than those in the curves for TiS_2 . IR drops in the electrolyte etc. can be considered as approximately

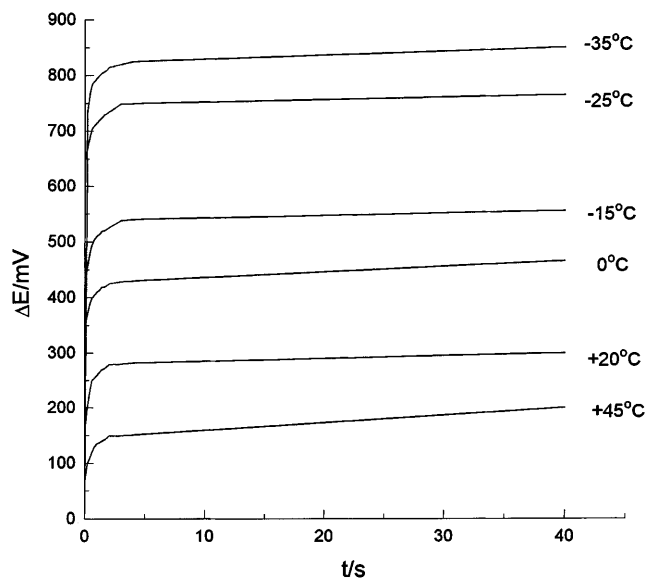


Fig. 3 Galvanostatic switch-on curves in electrolyte no. 1 at various temperatures; current density is 8 mA/g or ca. $1.5 \text{ mA}/\text{cm}^2$

equal, and therefore the difference in the potential jumps must be associated with the slowness of Li^+ discharge on the carbon surface and/or with an additive IR-drop in the surface film on the carbon electrodes.

According to the theory of chronopotentiometry, the dependence of Li concentration at the surface (c_s) at time t obeys the following equation:

$$c_s = c_s^0 \pm \frac{2i}{F} \sqrt{\frac{t}{\pi D}} \quad (2)$$

where c_s^0 is the initial concentration, D is the diffusion coefficient, i is the true current density, the sign “+” corresponds to a cathodic process, and the sign “-” to an anodic one.

The values of c_s and c_s^0 are related to corresponding values of x_s and x_s^0 by obvious equations

$$x_s = c_s/c^*; \quad x_s^0 = c_s^0/c^* \quad (3)$$

where c^* is the Li concentration in LiC_6 , i.e. $0.03 \text{ mol} \cdot \text{cm}^{-3}$.

Therefore

$$x_s = x_s^0 \pm \frac{2i}{c^*F} \sqrt{\frac{t}{\pi D}} \quad (4)$$

As was shown in [4], the dependence of o.c.p on x can be expressed as

$$E = -\frac{RT}{F} \ln \gamma - \frac{nRT}{F} \ln x \quad (5)$$

where constants γ and n are slightly dependent on the nature of the electrolyte.

Combination of (4) and (5) results in

$$E = E_0 - \frac{nRT}{F} \ln \left\{ x_s^0 \pm \frac{2i}{c^*F} \sqrt{\frac{t}{\pi D}} \right\} \quad (6)$$

where $E_0 \equiv -\frac{RT}{F} \ln \gamma$.

Equation 6 can be substantially simplified for short diffusion times, namely where

$$\frac{2i}{x_s^0 c^* F} \sqrt{\frac{t}{\pi D}} \ll 1 \quad (7)$$

In this case

$$E \cong E_0 - \frac{nRT}{F} \ln x_s^0 + \frac{-2inRT}{x_s^0 c^* F^2} \sqrt{\frac{t}{\pi D}} \quad (8)$$

An estimation showed that Eq. 8 must be valid at all real times of experiments; therefore switch-on curves can be linearized by using E, \sqrt{t} -co-ordinates. One example of the linearization is shown in Fig. 4. Extrapolation of straight lines to $t \rightarrow 0$ gives the possibility to determine the initial potential jump more precisely. The slopes of these straight lines are proportional to current, according to Eq. 8.

Figure 5 shows the polarization curves of the anodic process (lithium deintercalation) in electrolyte no. 1 at temperatures from -35 to $+45$ °C. These curves are

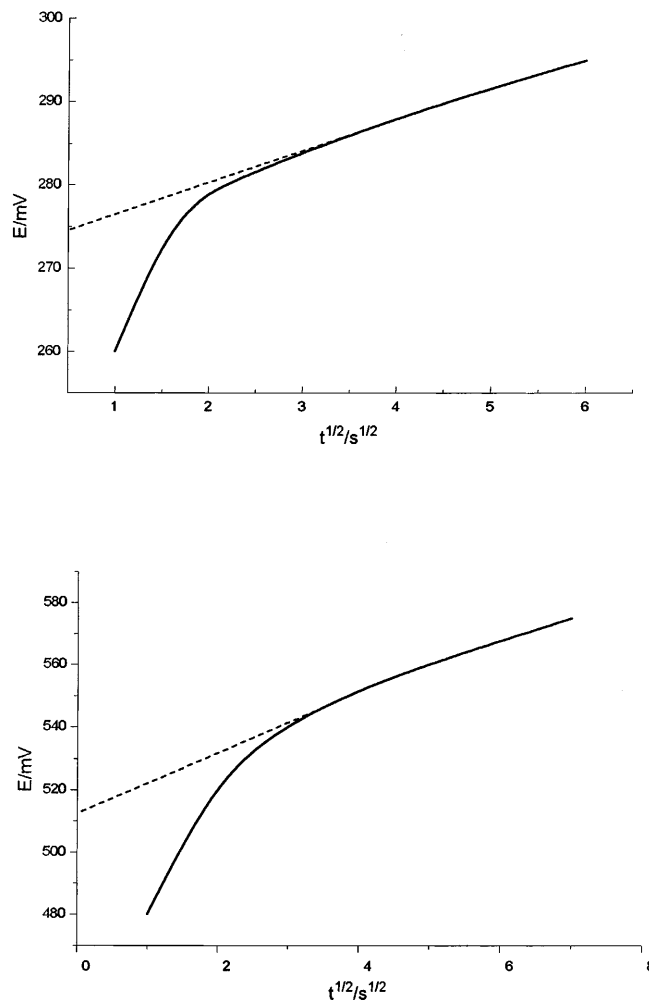


Fig. 4 Switch-on curves in co-ordinates $E, t^{1/2}$ in electrolyte no. 1 at 20°C for currents 2.5 mA (top) and 5 mA (bottom)

functions of current density on initial potential jumps of switch-on curves. Therefore, the overpotential in this case is the sum of the activation polarization and the ohmic drop. The polarization curves in electrolyte no. 3 are shown in Fig. 6.

It can be seen that all polarization curves are linear at fairly high temperatures. This denotes that the activation polarization in this case was rather low, not more than a few millivolts. The temperature decrease results in the growth of activation polarization, and the polarization curves become non-linear.

The initial slope of the polarization curves $(dE/dI)_{I \rightarrow 0}$ corresponds to sum of the polarization and ohmic resistances. The temperature dependence of this slope allows us to calculate some effective activation energy. For all electrolytes studied the effective activation energy was ca. $20 \text{ kJ} \cdot \text{mol}^{-1}$. This value is more than the activation energy of the electrolyte conductivity [5]. Therefore, this value is associated with the slowness of the intrinsic electrochemical stage of process. It is interesting to note the very small influence of the nature of the electrolyte on the activation energy.

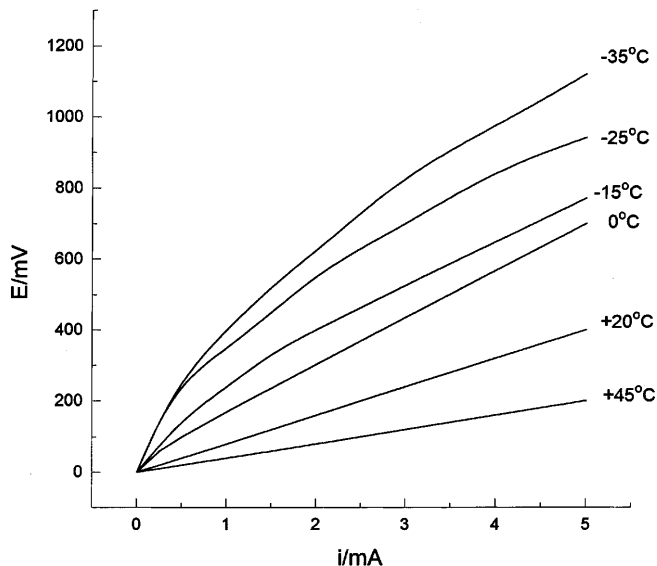


Fig. 5 Polarization curves of the anodic process in electrolyte no. 1 at various temperatures

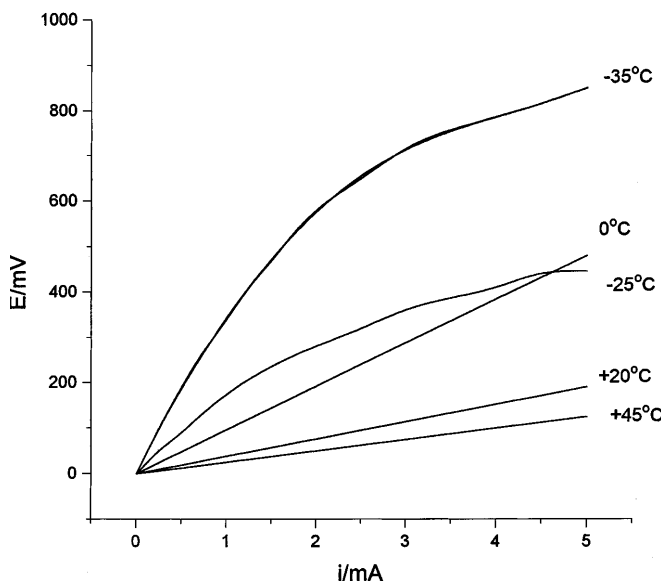


Fig. 6 Polarization curves of the anodic process in electrolyte no. 3 at various temperatures

Corrosion of the intercalate

It was mentioned above that the o.c.p. of the Li intercalate drifted in the positive direction, and that this drift was associated with corrosion. The corrosion of an intercalate may be considered as two coupled processes, namely, anodic lithium dissolution from the intercalate and cathodic reduction on the intercalate surface. Reducing species can be, in principle, solvent, anion, and more likely, electrolyte impurities, e.g. water traces. As corrosion results in depletion of intercalate by lithium, measurement of the o.c.p. drift can be used as a very convenient method for determination of corrosion rate.

Indeed, in the case under consideration, variation of the o.c.p. E with time t is related to variation of the degree of intercalation x :

$$dE/dt = (dE/dx)(dx/dt) \quad (9)$$

Equation 9 is valid on condition that solid-state diffusion of lithium in the intercalate bulk is fast in comparison with the corrosion rate, i.e. that the distribution of the Li concentration through the intercalate is uniform.

The degree of intercalation is related to the charge Q by:

$$x = Q/Q^* \quad (10)$$

where $Q^* = 372 \text{ mAh/g}$ (corresponding to LiC_6). So, the corrosion current $i_{\text{corr.}} \equiv -dQ/dt$ can be expressed by:

$$i_{\text{corr.}} = -Q^*(dE/dt)/(dE/dx) \quad (11)$$

The value of dE/dx is the slope of the equilibrium dependence of potential on degree of intercalation. Taking into account Eq. 5, we may conclude that in the case of lithium intercalation into carbonaceous materials

$$dE/dx = -nRT/xF \quad (12)$$

and therefore

$$i_{\text{corr.}} = -Q^*xF \frac{dE/dt}{nRT} \quad (13)$$

Table 1 contains the data on corrosion rates under various conditions.

It can be seen that the corrosion kinetics is slightly dependent on the nature of the electrolyte and the degree of intercalation, but strongly dependent on the temperature.

An apparent activation energy of corrosion W_a was estimated from the data of Table 1 with the aid of the equation

$$a = \frac{RT_1T_2(\ln i_1 - \ln i_2)}{T_1 - T_2} \quad (14)$$

where T_1 and T_2 are absolute temperatures, and i_1 and i_2 are corrosion rates at these temperatures. Values of W_a calculated for $T_1 = 318 \text{ K}$ and $T_2 = 298 \text{ K}$ are $155 \text{ kJ} \cdot \text{mol}^{-1}$ for electrolyte no. 1, $130 \text{ kJ} \cdot \text{mol}^{-1}$ for electrolyte no. 2, and $120 \text{ kJ} \cdot \text{mol}^{-1}$ for electrolyte no. 3. Such high values of W_a suggest that corrosion is controlled by the rate of the cathodic process.

It can be seen from Table 1 that the corrosion rate at 20°C is actually very low; it is less than the current in the experiments for the determination of the equilibrium E, x dependences in [4] (ca. $0.1 \text{ mA} \cdot \text{g}^{-1}$). Therefore, in this case, the composition of the intercalate (i.e., x) may be considered as uniform through the whole sample body. At the same time, the corrosion rate at 45°C is rather high, and the distribution of x through the sample cannot be uniform. Non-uniformity of the distribution of x results in an apparent lowering of Q^* and, therefore, an apparent

Table 1 Corrosion rates of intercalates in various electrolytes

Electrolyte no.	Degree of intercalation	Temperature/°C	O.c.p. shift/mV · hour ⁻¹	Corrosion rate/mA · g ⁻¹
1	0.1	20	0.17	0.0075
1	0.7	20	0.017	0.012
1	0.7	45	2.7	1.69
2	0.1	20	0.53	0.025
2	0.7	20	0.045	0.043
2	0.7	45	3.3	2.85
3	0.1	20	0.68	0.038
3	0.7	20	0.057	0.052
3	0.7	45	3.1	2.57

increase in the corrosion rate. It was found in our previous measurements that an increase in current density up to 2 mA/g resulted in a 1.5-fold decrease of real intercalation capacity. Therefore, an apparent increase of corrosion rate can also be estimated as 1.5-fold. On the other hand, a 1.5-fold increase in the corrosion rate at 45 °C results in an apparent increase in W_a of ca. 13 kJ/mol, although this does not alter the main conclusion.

The authors of [6] reported the results of the measurement of corrosion rate of a lithium-petroleum coke intercalate in 1 M LiCF₃SO₃ in a mixture of PC-ethylene carbonate (EC)-dimethylcarbonate (DMC) at 45 °C. The corrosion rate at $x = 0.7$ was about 0.05-0.07 mA/g. These figures are lower than the data of Table 1. The difference may be due to the difference in the nature of the electrolyte as well as to the difference in the carbon materials studied. Recently it was shown [7] that the corrosion rate of lithiated coke in solutions of LiPF₆ in different solvents is strongly dependent on the nature of the solvent, and increases in the order PC-EC – PC-DME – PC-DMC.

Conclusions

In spite of the importance of lithium intercalation into carbon materials, the influence of temperature on this process has not been studied previously. The present work aimed to study lithium intercalation from various non-aqueous electrolytes into carbonized cloth over a wide temperature range.

Increase of temperature from –35 to +45 °C results in a shift of the open-circuit potential (o.c.p.) of the lithium intercalates in the negative direction, this shift

being more pronounced at lower temperatures. The average temperature coefficient of the o.c.p. is equal to $-0.04 \text{ mV} \cdot \text{K}^{-1}$ and the corresponding entropy change for the lithium intercalation is about $12 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

The kinetics of intercalation and deintercalation is substantially dependent on temperature. At room and higher temperatures these processes are quasi-ohmic; at lower temperatures they have mixed activation-ohmic control. The effective activation energy of these processes is about $20 \text{ kJ} \cdot \text{mol}^{-1}$.

It was shown that intercalates are corroded in all the electrolytes studied the corrosion rate being increased as the temperature is raised. The apparent activation energy of corrosion is much greater than that of intercalation. It is suggested that the limiting step of corrosion is cathodic reduction of the components of the electrolytes.

References

1. Yazami R, Zaghbi K, Deschamps M (1994) *J Power Sources* 52: 55
2. MacLean GK, Aiken PA, Adams WA, Mussivand T (1995) *J Power Sources* 56: 69
3. Skundin AM, Stefanovskaya EE, and Egorkina OYu (1993) *J Power Sources* 43: 301
4. Skundin AM, Egorkina OYu (1995) *Russian Electrochemistry* 31: 373
5. Volkov OV, Kanevskii LS, Radchenko AF, Skundin AM (1991) *Soviet Electrochemistry* 27: 1198
6. Jean M, Tranchant A, Messina R (1996) *J Electrochem Soc* 143: 391
7. Von Sacken U, Nodwell E, Sundher A, Dahn JR (1994) *Solid State Ionics* 69: 284