

The use of accelerating rate calorimetry (ARC) for the study of the thermal reactions of Li-ion battery electrolyte solutions

J.S. Gnanaraj^a, E. Zinigrad^a, L. Asraf^a, H.E. Gottlieb^a,
M. Sprecher^a, D. Aurbach^{a,*}, M. Schmidt^b

^aDepartment of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

^bMerck KGaA, D-64293 Darmstadt, Germany

Abstract

The thermal stability of 1M LiPF₆, LiClO₄, LiN(SO₂CF₂CF₃)₂ (LiBETI) and LiPF₃(CF₂CF₃)₃ (LiFAP) solutions in mixtures of ethylene carbonate, diethyl carbonate and dimethyl carbonate in the temperature range 40–350 °C was studied by ARC and DSC. NMR was used to analyze the reaction products at different reaction stages. The least thermally stable are LiClO₄ solutions. LiPF₃(CF₂CF₃)₃ solutions showed higher thermal stability than LiPF₆ solutions. The highest thermal stability was found for LiN(SO₂CF₂CF₃)₂ solutions. Studies by DSC and pressure measurements during ARC experiments with LiPF₆ and LiFAP solutions detected an endothermic reaction, which occurs before a number of exothermic reactions as the temperature increases. Fluoride ions are formed and react with the alkyl carbonate molecules both as bases and as nucleophiles.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Accelerating rate calorimetry (ARC); Differential scanning calorimetry (DSC); Thermal stability; Alkyl carbonate solutions

1. Introduction

Accelerating rate calorimetry (ARC) is an important method for studying the thermal behavior of materials [1,2]. LiPF₆ solutions in alkyl carbonates are widely used in commercial Li-ion batteries in spite of their relatively low thermal stability. Recently, Merck KGaA introduced a new salt LiPF₃(CF₂CF₃)₃ (LiFAP) as an alternative electrolyte to LiPF₆. We explored the possibility of replacing LiPF₆ solutions by LiFAP solutions for Li ion batteries. In the present study ARC was used to explore endothermic and exothermic reactions of Li ion battery electrolyte solutions by monitoring both gas pressure and temperature responses. Differential scanning calorimetry (DSC) was also used to complement the thermal data obtained from the studies by ARC. Nuclear magnetic resonance (NMR) was used to analyze the products of the thermal reactions of the solutions.

In addition to the above two salts solutions, solutions containing LiClO₄ and LiN(SO₂CF₂CF₃)₂ (LiBETI) were also studied.

2. Experimental

One molar LiPF₆, LiClO₄, LiN(SO₂CF₂CF₃)₂ and LiPF₃(CF₂CF₃)₃ solutions in mixture of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) (2:1:2 v/v/v) were obtained from Merck KGaA (highly pure, Li battery grade).

Both an accelerating rate calorimeter (ARC, Arthur D Little Inc. Model 2000) and a differential scanning calorimeter (DSC, Mettler Toledo Inc. Model DSC 25) were used.

In the ARC tests the solutions were heated between 40 and 350 °C with 5 °C increments at the rate of 2 °C/min in the search for self-heating at the sensitivity threshold of 0.02 °C/min. The controller was programmed to wait 15 min for the sample and calorimeter temperatures to equilibrate, and then to search 20 min for a temperature increase of 0.02 °C/min. After ARC experiments the bomb was cooled with liquid nitrogen till the pressure was slightly above the atmospheric pressure. The gas was released through a high-pressure valve, specially designed for this purpose. DSC tests were carried out at a heating rate of 2 °C/min in the temperature range 30–400 °C. We have used ¹H, ¹³C, ³¹P and ¹⁹F NMR and GCMS to analyze the reaction products at different reaction stages. Two milliliters of a solvent mixture or a Li

* Corresponding author. Tel.: +972-3-5318317; fax: +972-3-5351250.
E-mail address: aurbach@mail.biu.ac.il (D. Aurbach).

salt solution were placed in a titanium spherical bomb (8 ml volume) in an argon filled glove box and were transferred to the ARC under a highly pure Ar atmosphere. High-pressure gold plated stainless crucibles, 30 μ l in volume, were used in the DSC tests. The crucibles were filled by three micro liters of a sample and were closed in the glove box.

3. Results and discussion

We measured both pressure and temperature rise during the decomposition reactions of the electrolyte solution. We identified both endothermic and exothermic reactions. The endothermic reactions could be identified by gas evolution with no exotherms in the ARC measurements and by DSC.

Fig. 1 shows the change in pressure measured when a solvent mixture and solutions containing different lithium salts were heated between 40 and 350 $^{\circ}$ C. The minor pressure increase, which starts near 60 $^{\circ}$ C (Fig. 1), cannot be related to any chemical interaction between salts and the solvents because solvents without salt show exactly the same behavior (Fig. 1). The pure solvents mixture shows a significant pressure increase near 250 $^{\circ}$ C while some electrolyte solutions show a remarkable change in pressure below 200 $^{\circ}$ C. We suggest that all salts react with the solvents leading to the formation of gaseous products.

Explosion was observed with lithium perchlorate solution near 220 $^{\circ}$ C, resulting in the formation of small black particles inside the pipes of the pressure measuring system. The smallest pressure increase (about 110 psi) was measured with the LiBETI solution.

Solutions containing LiPF₆ developed the highest pressure (about 1700 psi) during the heating tests by ARC and the lowest temperature onset, around 170 $^{\circ}$ C, for the first process, which develops pressure, when compared to other electrolyte solutions. The pressure versus T plot for the LiFAP solution is similar to that for the LiPF₆ solution. However, the onset of the pressure development is 30 $^{\circ}$ C

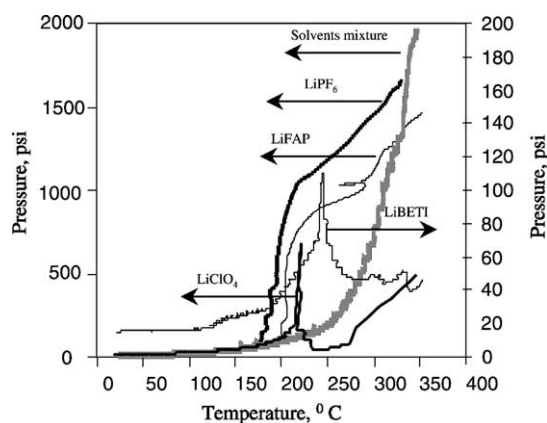


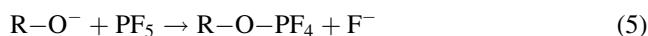
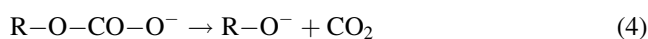
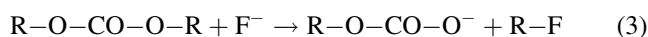
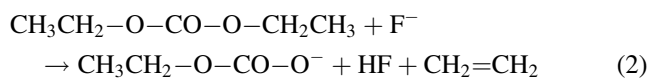
Fig. 1. Pressure vs. temperature profiles for 1M LiPF₆, LiPF₃(CF₂CF₃)₃, LiClO₄ and LiN(SO₂CF₂CF₃)₂ solutions in a mixture of EC:DEC:DMC (2:1:2 v/v/v) and for the solvents mixture without Li salt.

higher and the maximal pressure is 200 psi lower for the LiFAP solution than for the LiPF₆ solution.

A small exotherm between 325 and 350 $^{\circ}$ C and one process with a pressure development between 250 and 350 $^{\circ}$ C were detected upon heating the solvent mixture (Fig. 2). The exothermic reaction of the LiClO₄ solution with its onset at 220 $^{\circ}$ C (Fig. 2c) leads to an explosion. The highest thermal stability was found with the LiBETI solutions, which have the highest exothermic onset at 230 $^{\circ}$ C and the lowest self-heating rate (about of 1 $^{\circ}$ C/min). Exothermic decomposition of the LiFAP solution starts at temperatures only 10 $^{\circ}$ C higher than that of LiPF₆ solutions however the self-heating rate of the LiFAP solutions is considerably higher in the temperature range 210–290 $^{\circ}$ C (Fig. 2a and b). NMR measurements of the thermal reaction products indicate higher thermal stability of the P–F bonds in LiFAP solutions than the P–F bonds of LiPF₆ solutions. DSC measurements (Fig. 3) correlate well with both the NMR and the ARC measurements showing higher thermal stability of LiFAP solutions than of LiPF₆ solutions. The DSC measurements also showed that the LiBETI solutions have the highest thermal stability.

The lowest onset (200 $^{\circ}$ C) for an exothermic reaction was observed for LiPF₆ solutions. Fig. 2a shows a self-heating rate (SHR) with a maximum value of 5.4 $^{\circ}$ C/min and a pressure development rate (PDR) with a maximum value of 32 psi/min when LiPF₆ solutions are heated during ARC tests. It is clear from Figs. 1 and 2 that while the exothermic reactions of LiPF₆ solutions start at 200 $^{\circ}$ C there are two processes in which pressure is developed: the process which starts at 170 $^{\circ}$ C and during the exothermic reaction which starts above 200 $^{\circ}$ C.

The pressure rise at 170 $^{\circ}$ C can be attributed not only to the release of PF₅ from the PF₆[−] (Eq. (1)) but also to the production of ethylene from DEC, in an elimination reaction with fluoride ion acting as a strong base in aprotic solvent (Eq. (2)). The occurrence of this elimination explains the loss of condensed material during the reaction as well as the significantly lower stability of DEC solutions when compared to EC or DMC solutions [3–5].



Concentrating on the LiPF₆ solutions, the pressure build up starts at 170 $^{\circ}$ C (Figs. 1 and 2a) and the pressure development rate (PDR) versus T plot shows a peak at ca. 210 $^{\circ}$ C (Figs. 1 and 2a). The SHR versus T plots however show no peak before 190 $^{\circ}$ C. It is clear from the NMR results that most of the species with P–F bonds still exist and are stable at temperatures below 180 $^{\circ}$ C. At 180 $^{\circ}$ C, there is a

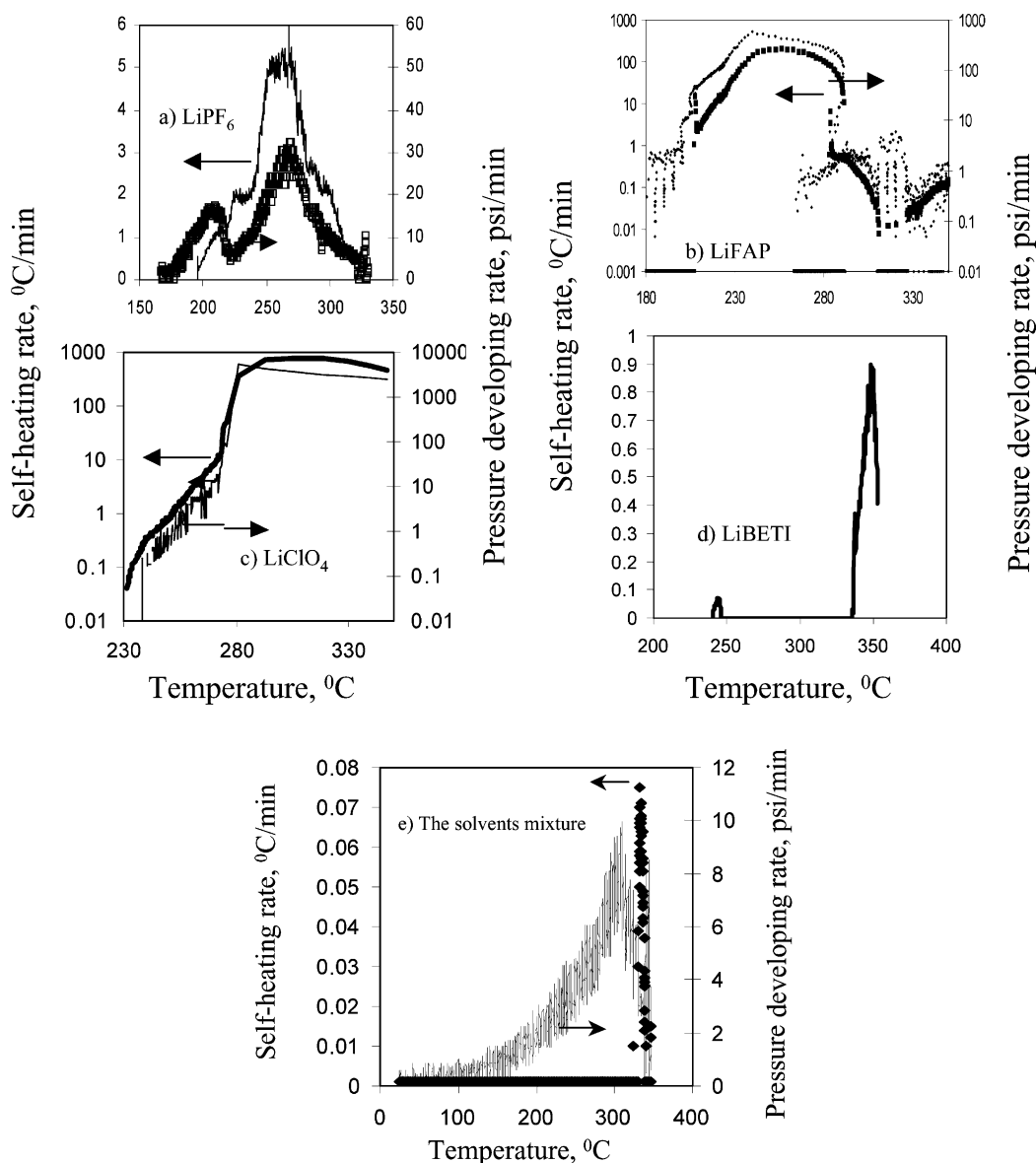


Fig. 2. Self-heating rate and pressure developing rate profiles for 1M electrolyte solutions in EC:DEC:DMC (2:1:2 v/v/v): (a) LiPF_6 ; (b) $\text{LiPF}_3(\text{CF}_2\text{CF}_3)_3$; (c) LiClO_4 ; (d) $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$; (e) the solvents mixture with no salt added.

transesterification of dimethyl and diethyl carbonates leading to the formation of methyl ethyl carbonate. Traces of polymeric species are seen in the ^{31}P NMR spectra (broad peaks between -40 and 5 ppm). Under the conditions of the test (180 °C) 25% of the original materials usually decompose and yield 10% of new condensed products. The series of exothermic reaction begins around 190 °C and the corresponding pressure peak is seen in the self-heating rate (SHR) and pressure developing rate (PDR) versus T plots (see Fig. 2a). The proposed nature of these reactions is shown in Eqs. (3)–(5), where Eq. (3) is intended to represent also the ring opening of the EC molecules [3]. The other major new products, identified from the NMR data, were: $\text{OH}-\text{CH}_2\text{CH}_2\text{OH}$, $\text{F}-\text{CH}_2\text{CH}_2\text{OH}$ and $\text{F}-\text{CH}_2-\text{CH}_3$. The NMR data show that above 220 °C no species with P–F bonds

remain in the condensed phase and none of the original solvent molecules survive in the sample.

The third exothermic process between 240 and 280 °C for LiPF_6 solutions also involves gas evolution and is characterized by the highest self-heating and pressure formation rates. As seen in Fig. 2a, there are thermal reactions also at temperatures above 280 °C (poorly resolved in the ARC data). The specific heat of the third exothermic reaction of LiPF_6 solutions is 130 J/g and the total specific heat of exothermic decomposition processes of LiPF_6 solutions was found to be 460 J/g based on the ARC measurements.

The sensitivity of the DSC measurements greatly depends on the ratio between the heating and reaction rates and they are less sensitive than the ARC measurements for thermal

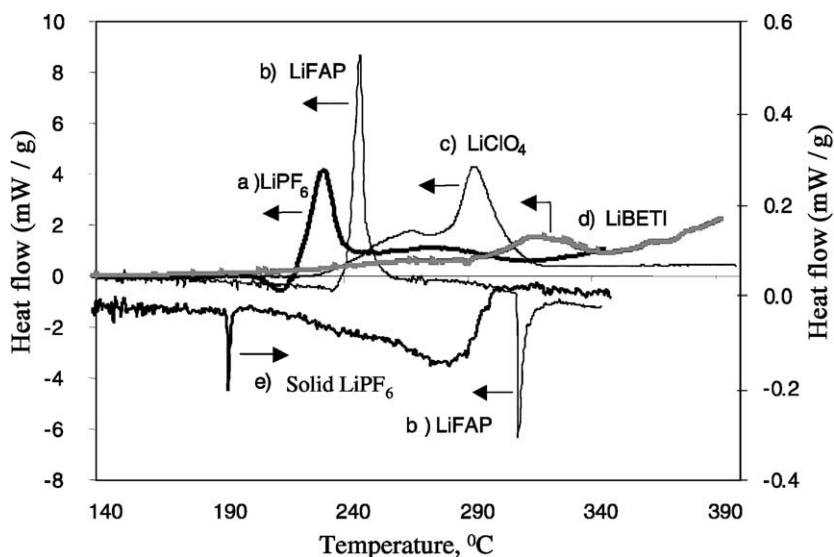


Fig. 3. DSC profiles for 1M solutions of: (a) LiPF_6 ; (b) $\text{LiPF}_3(\text{CF}_2\text{CF}_3)_3$; (c) LiClO_4 ; (d) $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ solutions in a mixture of EC:DEC:DMC (2:1:2 v/v) and (e) a DSC profile for solid LiPF_6 .

studies [1,2]. The DSC profiles for LiPF_6 and LiFAP solutions, at a heating rate of $2^\circ\text{C}/\text{min}$, show only three reactions with heat effects (Fig. 3). Endothermic peaks are also observed in the DSC curves with a shift of about 35°C compared to the ARC data between 205 and 220°C (Figs. 3 and 4). The endothermic peaks seen in Fig. 3 are in line with previously reported DSC data for the alkyl carbonate solutions containing LiPF_6 [5]. The exothermic peak, which is observed immediately after the endotherm, is relatively narrow, between 220 and 250°C , and is followed by a very broad exotherm between 250 and 315°C . Calculations of specific heat of reactions based on the DSC data gave 37 J/g for the endothermic reaction and 470 J/g for the exothermic reactions of the LiPF_6 solutions. Hence, the calculation of heat of reactions for LiPF_6 solutions based on the DSC and the ARC data nicely converge.

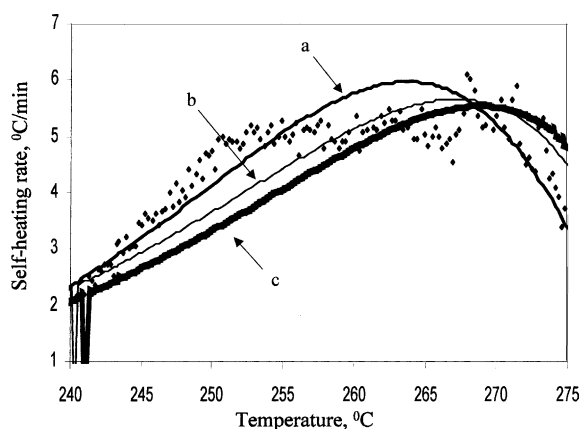
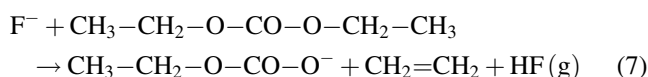
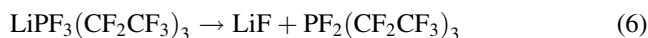


Fig. 4. Comparison of calculated self-heating rate profiles (solid lines) with the experimental data (points) for the third exothermic process of 1M LiPF_6 EC:DEC:DMC (2:1:2 v/v) electrolyte solution: (a) second order reaction, $E_a = 240\text{ kJ/mol}$; (b) first order reaction, $E_a = 165\text{ kJ/mol}$; (c) reaction of an order of 0.8, $E_a = 155\text{ kJ/mol}$.

Our DSC data for solid LiPF_6 salt (Fig. 3e) correlate with the report of Z. Zhang et al. [6], which observed endothermic reactions above 250°C using DSC (hermetically sealed aluminum cells). It is very important to take into account that both the ARC and the DSC measurements were carried out in hermetically closed vessels. Thermogravimetric analysis of the LiPF_6 in opened vessels under flowing nitrogen shows that a fast decomposition of the salt starts already at 70°C [7]. The PF_5 gas formed by this reaction (Eq. (1)) increases the pressure in the closed volume and forces the equilibrium (Eq. (1)) to the left. Hence, the decomposition rate is very low at room temperature and can be detected only at elevated temperatures.

At the respective temperature at which they occur, the exothermic reactions are one order of magnitude faster for LiFAP solutions than for LiPF_6 solutions. The heats of reaction for the thermal decomposition of the two solutions are similar.

Despite the difference in decomposition temperatures, in the case of LiPF_6 solutions as in the case of LiFAP solutions the electrolyte induces the decomposition of the solvent with gas evolution. We suggest that the first slow endothermic reaction detected by the ARC pressure measurements is similar to that of LiPF_6 electrolyte solutions (cf. Eqs. (1), (2), (6) and (7))



In addition to being a strong base in aprotic solution fluoride ion may act as a nucleophile attacking the alkyl carbonates and yielding alkyl fluorides and reactive mono-alkyl carbonates (Eqs. (3)–(5)). The superior thermal stability of LiFAP may be attributed to the electron attracting

property of the perfluoroalkyl groups, which raise the temperature required for fluoride ion release. Further mechanistic studies of these reactions are under way.

Using ARC calculation programs we obtained predicted SHR versus T curves for the third exothermic reaction of LiPF_6 solution, which takes place in the range 240–280 °C (Fig. 4) and compared them with the experimental results (Fig. 2a). We calculated SHR versus T plots for reactions of different orders. The best fit was obtained for a second order reaction with an activation energy of 240 kJ/mol. This relatively high value of the activation energy means that this high-pressure reaction is kinetically controlled. Further studies with LiBETI solutions are in progress.

4. Conclusion

Studies of the thermal behavior of the LiPF_6 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ and LiFAP solutions in a mixture of EC, DMC and DEC by ARC and DSC indicated that the LiPF_6 solutions have the lowest thermal stability while LiBETI solutions show the highest thermal stability. The LiBETI solutions show no changes in their composition at temperatures as high as 350 °C. The LiClO_4 solutions seem to be explosive as found by the ARC experiments: explosion of heated LiClO_4 solutions occurred above 220 °C.

Studies of the thermal behavior of the commercially used EC-DMC-DEC/ LiPF_6 solutions by ARC, detected one endothermic reaction starting about 170 °C, followed by at least five exothermic reactions in the temperature range 170–330 °C. DSC detected one endothermic and two exothermic reactions in the same range (200–350 °C) when using a heating rate of 2 °C/min.

LiPF_6 plays a major role in the thermal decomposition of the solution components in both the endothermic and the exothermic reactions. The endothermic process detected by the DSC measurements and by the pressure data from the ARC studies is proposed to involve an elimination reaction of DEC by F^- as a base. We found that the P–F bonds of the LiPF_6 or PF_5 are stable up to 180 °C and completely decompose at 220 °C. Most of the exothermic reactions detected, involve gas evolution and a build up of pressure due to the formation of HF, CO_2 and H_2O .

LiFAP solutions in commonly used alkyl carbonates have a higher thermal stability than LiPF_6 solutions, as is evident from the onset of both the endothermic and the exothermic decomposition reactions at higher temperatures and the lower pressure developed. At the temperature range from 210 to 290 °C the thermal decomposition of LiFAP solution is an order of magnitude faster than that of LiPF_6 solutions.

References

- [1] D.D. MacNeil, J.R. Dahn, J. Electrochem. Soc. 148 (2001) A1205.
- [2] D.D. MacNeil, D. Larcher, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 3596.
- [3] S. Mori, H. Asahina, H. Suzuki, A. Yonei, E. Yasukawa, J. Power Sources 68 (1997) 59.
- [4] T. Kawamura, A. Kimura, M. Egashira, S. Okada, J.I. Yamak, J. Power Sources 104 (2002) 260.
- [5] S.E. Sloop, J.K. Pugh, S. Wang, J.B. Kerr, K. Kinoshita, Electrochem. Solid Lett. 4 (2001) A42.
- [6] Z. Zhang, D. Fouchard, J.R. Rea, J. Power Sources 70 (1998) 16.
- [7] X. Zhang, P.N. Ross Jr., R. Kostecki, F. Kong, S. Sloop, J.B. Kerr, K. Striebel, E.J. Cairns, F. McLarnon, J. Electrochem. Soc. 148 (2001) A463.