Short communication

Lithium electrode reactants containing hydrogen or water

Robert A. Huggins *

Faculty of Engineering, University of Kiel, Kaiserstrasse 2, D-24143 Kiel, Germany

Abstract

The mechanisms whereby solid oxides can react with hydrogen and water are discussed. The potential range in which lithium-containing phases are stable in water can be calculated using the Gibbs triangle. Examples from the literature are cited.

Materials with potentials above the water stability window will tend to react with water vapor in the atmosphere, absorbing protons and electrons. High potential solids can also be used to extract lithium from aqueous solutions.

Experiments on the effect of the exposure of Pr_6O_{11} to water on the insertion of lithium are reported.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Lithium phases in water; Reaction with water vapor; High potential oxides; Water stability window; Lithium extraction from water

1. Introduction

It is generally known that alkali metals react vigorously with water, with the evolution of hydrogen. In addition, a number of materials containing lithium are sensitive to air and/or water, and thus have to be handled in dry rooms or glove boxes. Yet most of the lithium-containing oxides now used as positive electrode reactants in lithium battery systems are synthesized in air, often with little heed given to this problem. It is also known that hydrogen (protons) can be present in some oxides, and that both hydrogen and extra oxygen can be absorbed into oxides simultaneously in some cases.

The electrochemical insertion and deletion of electroactive species in solids has been of special interest in the electrochemical community for some three decades, since the demonstration of the possibility of the use of the insertion and deletion of lithium and other alkali metals in solid solutions as reversible electrodes in electrochemical cells [1–5]. This phenomena is now widely used in the electrodes of several types of batteries. Examples in which lithium ions are inserted or deleted are the so-called lithium-ion cells, which first became highly visible upon the introduction of the carbon/organic solvent electrolyte/$LiCoO_2$ system by Sony Energytec Inc. [6–9]. Electrochemical insertion and deletion of hydrogen

can also occur in battery electrodes. The use of metal hydrides as the negative electrode reactant, and the $Ni(OH)_2$/$NiOOH$ phase transformation as the positive electrode reactant, both in Hydride/Ni cells, are two prominent examples.

One can also use electrochemical methods to induce ion exchange, electrochemically introducing one species from the electrolyte, which can replace another species in the crystalline lattice. The species that is displaced leaves the solid and moves into the electrolyte or into another phase. This electrochemically-driven displacement process is now called "extrusion" by some investigators.

In addition to these electrochemically driven examples, there are several non-electrochemical methods by which the concentration of alkali metals or hydrogen in solids can be modified.

One of these is by chemically driven ion exchange, in which there is interdiffusion in the solid state between native ionic species and ionic species from an adjacent liquid phase. An example of this is the replacement of lithium ions in an oxide solid electrolyte or mixed-conductor by protons as the result of immersion in an acid solution. Protons from the solution diffuse into the oxide, replacing lithium ions, which move into the solution. The presence of anions in the solution that react with lithium ions to form stable products, such as LiCl, provides a strong driving force.

Instead of exchanging with lithium, hydrogen can be simply added to a solid in the form of interstitial protons. The

* Fax: +49 431 365 38.
  E-mail address: rhg@tf.uni-kiel.de.

charge balance requirement can be accomplished by the co-addition of either electronic or ionic species, i.e. either by the introduction of extra electrons or the introduction of negatively charged ionic species, such as O^{2-} ions. If electrons are introduced, the electrical potential of the material will become more negative, with a tendency toward n-type conductivity.

Similarly, oxygen, as oxide ions, can be introduced into solids, either directly from an adjacent gas phase or by reaction with water with the concurrent formation of gaseous hydrogen molecules. Oxide ions can generally not reside upon interstitial sites in dense oxides, and thus their introduction requires the presence of oxygen vacancies in the crystal lattice. If only negatively charged oxide ions are introduced, electroneutrality requires the introduction of electron holes. Thus, the electrical potential of the solid becomes more positive, with a tendency toward p-type conductivity.

There is another possibility, first discussed by Stotz and Wagner [10] and Wagner [11], that does not involve a change in the electrical potential. This is the simultaneous introduction of species related to both the hydrogen component and the oxygen component of water, i.e. both protons and oxide ions. This requires, of course, mechanisms for the transport of both hydrogen and oxygen species within the crystal structure, as well as the pre-existence of oxide ion vacancies. As mentioned above, the hydrogen enters the structure as mobile interstitial protons. In this case the electrical charge is balanced. Neither electrons nor holes are involved, so the electrical potential of the solid is not changed. The concurrent introduction of both protons and oxide ions is, of course, compositionally equivalent to the addition of water to the solid, although the species H_2O does not exist in the crystal structure.

In addition to a discussion of the conditions required for the presence of these phenomena in materials containing both lithium and hydrogen, experimental results on materials in the praseodymium–oxygen system will be presented, these involved electrochemical measurements on the insertion of lithium into PrO_x, both with and without prior reaction with water.

2. Thermodynamics of the lithium–water system

A number of the features of the interaction between lithium and hydrogen in solids can be understood in terms of the thermodynamics of the ternary Li–H–O system. A useful thinking tool that can be used for this purpose is the isothermal Gibbs triangle, in which the three elements are at the corners. The position of any point within the triangle represents the relative atomic fractions of the respective elements. If they can be assumed to have narrow ranges of compositions, the stable phases are represented by points along the edges or in the interior of the Gibbs triangle.

The basic triangle is divided into sub-triangles whose sides are defined by the stable two-phase tie lines between
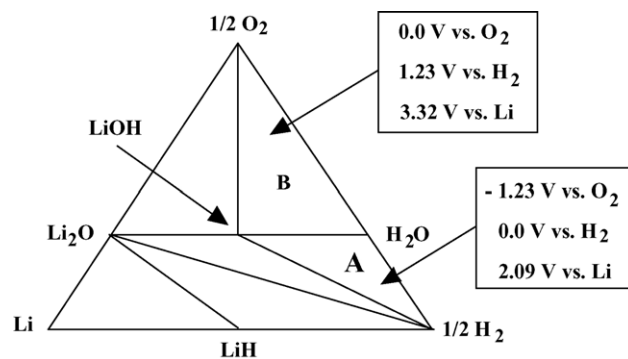

Fig. 1. Calculated phase stability diagram for the Li–H–O system, assuming unit activities of all phases.

the phases present. According to the Gibbs Phase Rule, all compositions within any given sub-triangle in such a ternary system have the same values of all intensive (amount-independent) thermodynamic parameters.

The Gibbs triangle for the Li–H–O system at ambient temperature that has been determined [12] by using chemical thermodynamic data from Barin [13] is shown in Fig. 1.

The calculated voltages for the potentials of all compositions in triangles A and B are shown relative to pure hydrogen, pure oxygen and lithium.

If one thinks in terms of an electrochemical cell with pure lithium at the negative electrode, the potential of water that is saturated with LiOH will be 2.09 V versus Li when hydrogen is present at one atmosphere. On the other hand, water saturated with LiOH will have a potential of 3.32 V versus Li if one atmosphere of oxygen is present. It can be seen that under these conditions water has a stability window of 1.23 V, as is the case in the binary hydrogen–oxygen system.

This also means that any lithium-containing material with a potential between 2.09 and 3.32 V versus Li will be stable in water. This is consistent with the fact that it has been empirically known for some time that materials with potentials more than 3.3 V versus Li are basically air-stable [14].

In the electrochemical literature potentials in aqueous solutions are often stated versus the standard hydrogen electrode, SHE. When this is done, the potentials of both pure hydrogen and pure oxygen vary with the pH. Their difference remains constant. Likewise, the potential of elementary Li in aqueous solutions varies with pH, so that the differences between the potentials of Li, H_2 and O_2 are pH-independent. This is consistent with the results of electrically neutral chemical thermodynamics discussed earlier.

3. Examples of phases containing lithium that are stable in water

A number of examples can be found in the literature that are consistent with, and illustrate these considerations. Particularly appropriate are several experimental results that were published by the group of J.R. Dahn some years ago.

They performed experiments on the addition of lithium to $LiMn_2O_4$ in a LiOH-containing aqueous electrolyte using a carbon negative electrode [15] and showed that the two-phase system $LiMn_2O_4$–$Li_2Mn_2O_4$, which is known to have a potential of 2.97 V versus Li [16] is stable in water containing LiOH.

They used a Ag/AgCl reference electrode, referred their measurements to the SHE, and then converted to the lithium scale, assuming that the potential of the lithium electrode is −3.05 V versus the SHE.

They found that lithium began reacting with the $LiMn_2O_4$ at a potential of −0.1 V versus the SHE, which is consistent with the reported value of 2.97 V versus Li. As lithium was added beyond the two-phase composition limit the potential fell to that for hydrogen evolution. They interpreted their data to give the hydrogen evolution at a potential 2.2 V versus pure Li, and predicted that oxygen evolution would occur on the carbon negative electrode at 3.4 V versus pure Li. It can readily be seen that these experimental results were consistent with the results of the Gibbs triangle calculations shown in Fig. 1.

The Dahn group also pointed out that the phase $VO_2(B)$ reacts with lithium at potentials within the stability range of water [17]. They performed electrochemical cell experiments in which $Li_xVO_2(B)$ acted as the negative electrode, and $Li_xMn_2O_4$ as the positive electrode. These aqueous electrolyte cells gave comparable results to those with the same electrodes in organic solvent electrolyte cells.

Additional experiments were done on the electrochemical behavior of $VO_2(B)$ in aqueous electrolytes by Zhang and Dahn [18]. They found that this material dissolves somewhat in electrolytes with high values of pH, and that the pH value influences the kinetics of the reaction with lithium, with hydrogen evolution and slower kinetics being found in the case of lower pH values.

4. Materials that have potentials above the stability window of water

At normal pressures materials with potentials more positive than that of pure oxygen will tend to oxidize water to cause the evolution of electrically neutral molecular oxygen gas. For this to happen there must be a concurrent reduction process. One possibility is the insertion of positively charged ionic species, along with their charge-balancing electrons, into the material in question. The insertion of protons or lithium ions and electrons into high-potential oxides is one possible example of such a reduction process. When this happens, the potential of the material goes toward that of pure oxygen.

4.1. Absorption of protons from water vapor in the atmosphere

A number of materials that are used as positive electrode reactants in lithium battery systems, such as $LiCoO_2$, $LiNiO_2$

and $LiMn_2O_4$, have operating potentials well above the stability range of water. Cells containing these materials and carbon negative electrodes are typically assembled in the uncharged state. It is generally found that the cell voltage at the start of the first charge is typically consistent with the expectation that the positive electrodes would have initial potentials comparable, or near to, that of air, somewhat over 3 V versus Li.

This can be explained by the reaction of these materials with water vapor in the atmosphere. Protons and electrons enter their crystal structures, reducing their potentials, accompanied by the concurrent evolution of molecular oxygen.

An example is a recent report [19] on the electrochemical behavior of $LiCoO_2$, a high potential electrode material that showed differences in the rate of high voltage capacity loss upon cycling between the samples that were treated in different ways so as to modify the influence of water. The authors attributed these effects to side reactions involving the formation of a surface layer involving moisture-related species.

4.2. Extraction of lithium from aqueous solutions

If a material that can insert lithium has a potential above or within the stability range of water, it can be used to extract lithium from aqueous solutions. This was demonstrated by experiments on the use of the λ-MnO_2 spinel phase that absorbed lithium when it was immersed in aqueous chloride solutions [20].

5. Experiments on materials in the praseodymium oxide system

5.1. Phases in the praseodymium oxide system

Whereas many of the common solid solutions contain randomly arranged isolated point defects, such as substitutional ions, vacancies or interstitials, there are others in which the defects are present in organized arrangements, sometimes with planar arrays of vacancies, and sometimes with two- or three-dimensional block structures composed of combinations of planar defects, This general class of materials is often said to contain "extended defects", and changes in their amounts and types can lead to a series of homologous compounds that are all related to a simple "mother" crystal structure. As examples, the families of homologous oxides of titanium and vanadium are derived from the rutile mother structure and the various oxides of molybdenum and tungsten are derived from the ReO_3 structure. Compositional variations occur by changes in the number and types of these organized defect structures, some of which can have remarkably high mobilities. Discussions of this general class of solids can be found in [21,22].

Table 1
Members of the homologous series Pr_nO_{2n-2}

Value of n	Formula	x in PrO_x	Average oxidation state of Pr
4	Pr_2O_3	1.5	3
7	Pr_7O_{12}	1.714	3.428
9	Pr_9O_{16}	1.778	3.556
10	Pr_5O_9	1.8	3.6
11	$Pr_{11}O_{20}$	1.818	3.636
12	Pr_6O_{11}	1.833	3.866
Infinity	PrO_2	2	4

The praseodymium oxide system is also of this general type. There are six sub-oxides that are all closely related to each other that are derived from the mother phase PrO_2, which has the fluorite structure. They form a homologous series whose compositions can be written as Pr_nO_{2n-2}. Materials in this binary system have been studied by several investigators [23–26].

The compositions of the various phases in the praseodymium–oxygen system are shown in Table 1, which shows their formulas, the ratio of oxygen/praseodymium and the average oxidation state of the praseodymium ions.

Experimental results are available in the literature from isobaric studies [23] and from high temperature X-ray diffraction information [24] that show the phase relationships as functions of temperature under isobaric conditions.

These materials react rapidly as either the temperature or the oxygen pressure is changed. This involves the reversible absorption of oxygen, presumably involving transport along the extended defect structure, rather than by the existence and motion of isolated point defects. In the case of other materials with similar extended defects, such changes have been directly observed in situ by electron microscopy. The especially rapid kinetics of oxygen insertion or removal in the praseodymium–oxygen system is indicated by the fact that it has been found that it is difficult to cool fast enough to freeze-in equilibrium compositions above about 350–400 °C [23]. Experimental information about the mixed ionic and electronic conductivity in some of these phases has been reported [27].

There are also indications that lithium can also have appreciable mobility in this material, and it has been investigated as a potential thin layer electrochromic material for use in eyeware [28]. It was found that the electronic conductivity is relatively high when the composition is near Pr_6O_{11}, which is dark, but decreases as lithium is added, and the color disappears. Several ternary Li–Pr–O phases are also known, including Li_2PrO_3 and Li_8PrO_6 [29]. The oxidation state of praseodymium is 4+ in both of these cases.

The praseodymium oxide system is unique in that the phase Pr_6O_{11} (or $PrO_{1.83}$), rather than the mother phase PrO_2, is stable at ambient temperatures in dry air. However, it has been observed that when moist air is present during the preparation, the phase PrO_2 is present in addition to the usual Pr_6O_{11}. Upon heating under vacuum to 270 °C, the PrO_2 is reduced to Pr_6O_{11} [25].

5.2. Experiments on PrO_x

Because of the unusual defect structure and mass transport properties of this family of materials, some experiments were undertaken to explore the insertion of lithium into the phase that is stable under ambient conditions, Pr_6O_{11}, and to see the influence of the presence of water.

The results of thermal analysis and X-ray diffraction studies, as well as coulometric titration experiments, have been reported elsewhere [30]. They showed an irreversible weight loss at about 300 °C upon heating an as-received sample that had been left in air for several months, and a much larger indication of the presence of water in a sample that had been boiled in water for 4 h. This evidence of the presence of water was not found in a sample that had been heated to 350 °C. The X-ray diffraction results coincided with reports in the literature that the presence of water was accompanied by the presence of some PrO_2.

Coulometric titration experiments were undertaken to evaluate the insertion of lithium into these materials using coffee bag electrochemical cell technology with an organic solvent electrolyte, and using elemental lithium as the counter electrode. In order to avoid complications due to the concurrent absorption of lithium into it, no carbon was added to the electrode to increase the electronic conduction.

The result of a coulometric titration experiment on a sample of Pr_6O_{11} (99.9% Pr_6O_{11} from ChemPur) that had been heated to 350 °C to expel water is shown in Fig. 2. Prior thermal analysis experiments showed a weight loss peak in the range of 250–325 °C. The potential started at somewhat over 3 V versus Li, which is typical for materials prepared in air, as mentioned earlier, and dropped as lithium was added. About 0.6 Li ions/mol of Pr_6O_{11} could be added in solid solution. When this concentration was exceeded, a second phase began to form, resulting in a potential plateau at about 2.0 V versus Li. This two-phase region extended to almost 2 Li/mol of Pr_6O_{11}.

A coulometric titration experiment was also performed on a sample of the as-received material that had been sitting in the laboratory air for several months. The results were quite
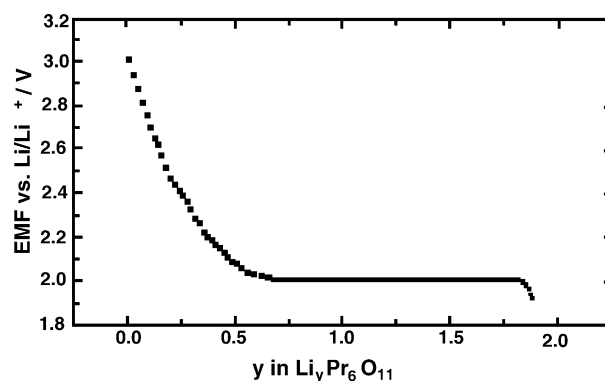

Fig. 2. Coulometric titration curve of sample of Pr_6O_{11} that had been heated to 350 °C to expel water.
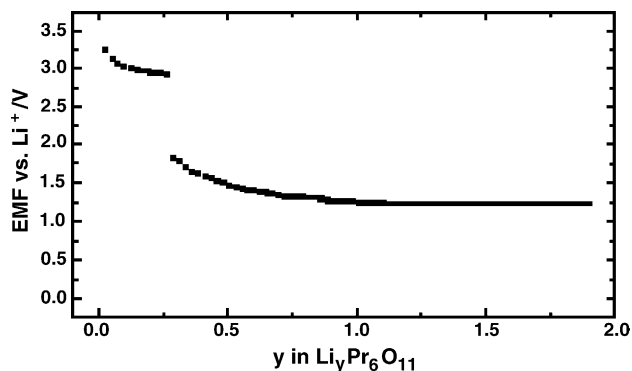
Fig. 3. Coulometric titration curve of sample of Pr_6O_{11} that had been exposed to laboratory air.

different, as shown in Fig. 3. Instead of having the characteristics of a single solid solution, those data indicate the absorption of about 0.25 Li at a high potential, and then a sudden drop to a much lower region, from somewhat below 2.0 V versus Li to an apparent plateau at about 1.25 V versus Li. The experiment had to be stopped before the composition limit of the plateau was reached, for the cell resistance became so high that it was difficult to obtain satisfactory voltage readings. Thus, we do not know the real composition limit of this plateau. This high resistance indicated that the electronic conductivity had decreased to a low value as the result of the introduction of the lithium.

In order to confirm that this difference was related to the presence of water, or reaction with water, another experiment was undertaken. In that case a sample of Pr_6O_{11} was boiled in water for several hours. The results in this case were similar to those on the sample that had been in laboratory air for some time. After starting over 3 V versus Li, the potential dropped gradually until about 0.25 Li per mol had been absorbed, whereupon it suddenly dropped to about 1.5 V, followed by a long plateau at about 1.25 V versus Li. These results are shown in Fig. 4.

These experiments clearly show that interaction with water has a large effect upon the electrochemical behavior of Pr_6O_{11} in a lithium cell. In the absence of water, the obser-

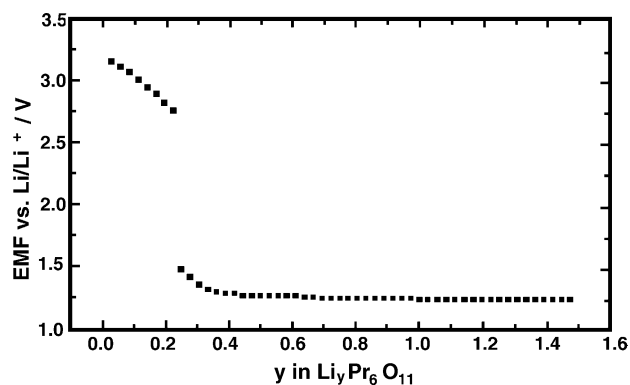vations indicate a normal single phase insertion reaction up to about 0.5 Li per mol of PrO_x, followed by a two-phase reconstitution reaction to form a second phase at a constant potential of about 2 V versus Li.

Upon interaction with water, which can involve the insertion of both protons and oxide ions into these materials, the picture is different. There are obviously two different reactions. The first occurs at potentials close to that of the formation of Li_2O from the elements, which is 2.91 V versus Li/Li^+ for unit activity oxygen at 298 K. Therefore, it is reasonable to assume that the higher voltage portion is related to the reaction of the initial lithium inserted into the structure with the oxide ions from the water.

The lower voltage part of the reaction, which was found at potentials lower than in the case of Pr_6O_{11} without water, must be related to the presence of the protons. If we can represent the composition of PrO_x containing some protons as H_yPrO_x, the displacement of the protons by lithium ions to form gaseous hydrogen can be written as

$$yLi + H_yPrO_x = Li_yPrO_x + (y/2)H_2 \qquad (1)$$
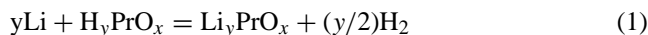
The potential of this displacement reaction is determined by the difference in the Gibbs free energies of formation of the two phases Li_yPrO_x and H_yPrO_x. It must, therefore, be lower than the reaction with lithium alone, as was found in these experiments. Additional experiments will have to be undertaken in the future to help further understand these effects.

6. Concluding remarks

Both lithium and protons can be inserted into a number of materials that are interesting as battery electrode reactants. This can occur under both chemical and electrochemical conditions. The presence of protons can have large effects upon the behavior of both positive and negative lithium electrode materials.

In materials containing lithium a critical feature is the electrochemical potential and its relationship to the stability window of water, which can be readily calculated from electrically neutral chemical thermodynamics.

Materials with high potentials will tend to react with water vapor in their environments, and can also be used to extract lithium from aqueous solutions.

Experiments on the influence of the exposure to water upon the subsequent reaction of Pr_6O_{11} with lithium illustrate such effects.

References

[1] M.S. Whittingham, R.A. Huggins, J. Chem. Phys. 54 (1971) 414.
[2] M.S. Whittingham, R.A. Huggins, in: R.S. Roth, S.J. Schneider Jr. (Eds.), Solid State Chemistry, vol. 364, National Bureau of Standards Special Publication, 1972, p. 139.
[3] M.S. Whittingham, R.A. Huggins, in: W. van Gool (Ed.), Fast Ion Transport in Solids, North-Holland, 1973, p. 645.

Fig. 4. Coulometric titration curve of sample of Pr_6O_{11} that had been boiled in water.

[4] B.C.H. Steele, W. van Gool (Eds.), Fast Ion Transport in Solids, North-Holland, 1973, p. 103.

[5] M.B. Armand, in: W. van Gool (Ed.), Fast Ion Transport in Solids, North-Holland, 1973, p. 665.

[6] T. Nagaura, Presentation at Third International Rechargeable Battery Seminar, Deerfield Beach, FL, USA, 1990.

[7] T. Nagaura, J. Electron. Ind. (1990) 45.

[8] T. Nagaura, K. Tozawa, Progr. Batteries Solar Cells 9 (1990) 209.

[9] T. Nagaura, Prog. Batteries Battery Mater. 10 (1991) 218.

[10] S. Stotz, C. Wagner, Ber. Bunsenges. Phys. Chem. 70 (1966) 781.

[11] C. Wagner, Ber. Bunsenges. Phys. Chem. 72 (1968) 778.

[12] R.A. Huggins, Solid State Ionics 136–137 (2000) 1321.

[13] I. Barin, Thermochemical Data of Pure Substances, VCH Verlag, 1989.

[14] J.R. Dahn, U. von Sacken, H. Al-Janaby, M.W. Juzkow, J. Electrochem. Soc. 138 (1991) 2207.

[15] W. Li, W.R. McKinnon, J.R. Dahn, J. Electrochem. Soc. 141 (1994) 2310.

[16] J.M. Tarascon, D. Guyomard, J. Electrochem. Soc. 138 (1993) 2864.

[17] W. Li, J.R. Dahn, J. Electrochem. Soc. 142 (1995) 1742.

[18] M. Zhang, J.R. Dahn, J. Electrochem. Soc. 143 (1996) 2730.

[19] Z. Chen, J.R. Dahn, Electrochem. Solid-State Lett. 7 (2004) 11.

[20] H. Kanoh, K. Ooi, Y. Miyai, S. Katoh, Sep. Sci. Technol. 28 (1993) 643.

[21] L. Eyring, M. O'Keeffe, The Chemistry of Extended Defects in Non-metallic Solids, North-Holland, 1970.

[22] K. Kosuge, Chemistry of Non-stoichiometric Compounds, Oxford University Press, 1994.

[23] B.G. Hyde, D.J.M. Bevan, L. Eyring, Phil. Trans. R. Soc. A259 (1966) 583.

[24] U. Lott, PhD Thesis, University of Karlsruhe, 1968.

[25] D.A. Burnham, L. Eyring, J. Phys. Chem. 72 (1968) 4415.

[26] J. Kordis, L. Eyring, J. Phys. Chem. 72 (1968) 2044.

[27] V. Thangadurai, R.A. Huggins, W. Weppner, J. Solid State Electrochem. 5 (2001) 531.

[28] W.R. Kallman, Personal communication, Eyeonics Corp., Tualatin, OR, USA.

[29] R. Wolf, R. Hoppe, J. Solid State Chem. 70 (1987) 12.

[30] A. Netz, W.F. Chu, V. Thangadurai, R.A. Huggins, W. Weppner, Ionics 5 (1999) 426.