

SOME ASPECTS OF LITHIUM-COPPER COMPOUND CELLS IN LiCl-KCl EUTECTIC

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Summary

The electrochemical behaviour of cupric and cuprous sulphide in LiCl-KCl eutectic and possible side reactions thereof were investigated. These sulphides are valuable electrode materials showing reversible behaviour during cycling. Formation of cuprous sulphide occurs if metallic copper and cupric sulphide are present together in the eutectic. Nevertheless, there seems to be a re-formation of the starting material (cupric sulphide or a defined cupric-cuprous sulphide mixture are formed in the original or a very similar composition during re-oxidation). Because of the similar potentials of the sulphides only one voltage plateau is observed during discharge. The formation of highly soluble copper chlorides and sulphur occurs at potentials well above that of the copper sulphide re-formation and therefore causes no problems.

Introduction

The application of sulphur and some transition metal sulphides in cells using non-aqueous, organic solvents has been tested in the last ten years [1 - 3]. Because only rather low current densities are achieved in such cells, at the present time research is mainly focused on other systems *e.g.* on the sodium-sulphur cell, using a β -alumina electrolyte at operating temperatures of about 300 °C [4, 5], and systems using a liquid LiCl-KCl eutectic at temperatures near 450 °C. One active material used frequently in such melts was elemental sulphur [6, 7]. Because of the generation of soluble sulphide and polysulphide species [8 - 12] during discharge, the application of transition metal sulphides such as cupric sulphide [13] and iron sulphide [14 - 18] was suggested. However, up to now knowledge of the discharge behaviour and reaction mechanisms of the active materials in those cells is scant. Therefore, it seemed useful to investigate the behaviour of some copper compounds (especially the copper sulphides) in the eutectic and to compare

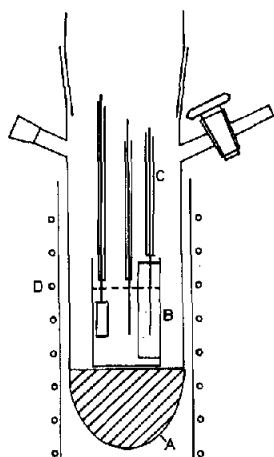


Fig. 1. Experimental quartz cell: (A) molecular sieves; (B) alumina crucible; (C) alumina tubes; (D) furnace.

some of the results with those obtained in non-aqueous, organic solvent systems.

Experimental

For the electrochemical experiments the measuring equipment shown in Fig. 1 was used. The outer housing of the cell was a closed quartz tube to allow experiments under vacuum or dry argon. The counter electrode was separated from the others by an alumina tube that was fastened at the wall of the crucible and open at both ends to avoid introduction of anodically produced chlorine into the melt. For measurements with cathodic currents at the measuring electrode, a graphite counter electrode was used (platinum counter electrodes readily dissolve because of the formation of platinum chloro-complexes). For cycling curves, however, a platinum counter electrode was used, because if graphite is kept at cathodic potentials in the melt, it is rapidly destroyed by intercalation of the alkali metal. The electrodes were spot-welded onto platinum wire leads. The reference electrode was a silver wire, working as an Ag/Ag^+ reference electrode.

Measuring equipment

For cyclic voltammetry a Wenking type potentiostat (68 TS 10), a voltage scan generator (VSG 72, G. Bank, Göttingen) and a Hewlett-Packard XY-recorder (HP 7004B) were used. The galvanostatic reduction curves were recorded by using a Wenking type potentiostat (70 TS 1) and an XT-recorder (Linseis). The curves given in the Figs. are not iR corrected. The current densities should be taken only as approximate values for the exact area of the electrodes cannot be determined by simply measuring the geometric areas.

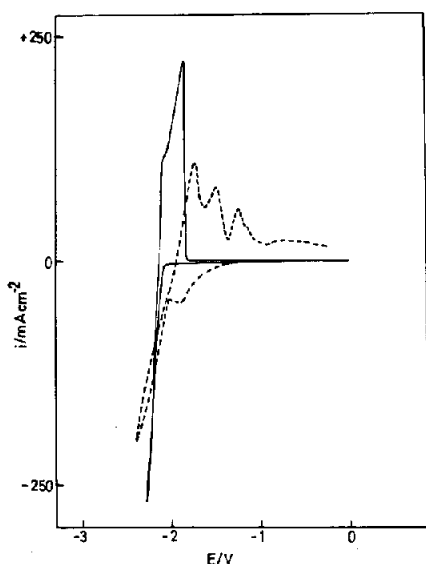


Fig. 2. Alkali metal deposition from LiCl-KCl eutectic; measuring electrode, copper; ----, measuring electrode: platinum screen. Scan rate: 5 mV/s; counter electrode: graphite; ref.: Ag/Ag⁺.

Cupric sulphide was made according to ref. [19] and had a copper content of 66.53% (average value from three determinations [20]). The theoretical copper value is 66.46%. Cuprous sulphide was obtained from Alfa Inorganics. The copper content (three determinations) was 78.2% (theoretical value: 79.85%). This lower value may be due to some cupric sulphide or sulphur impurities.

The eutectic was made by weighing the corresponding amounts of LiCl (59m/o) (Merck, p.a.) and KCl (Merck, p.a.), drying the mixture thoroughly at 180 °C under high vacuum and melting under vacuum. The eutectic was held at a temperature of about 400 °C. The measuring electrodes were made by folding a platinum or nickel screen (only for cathodic curves) and filling the pocket thus formed with the active material. The substances were then pressed onto the screen at a pressure of about 12,000 kg/cm².

Results

Before measuring copper sulphide samples the alkali metal deposition, the background current and the electroactive region of the eutectic were determined. The electroactive region is about 3.2 V under these conditions [determined from cyclic voltammograms (c.v.) at a platinum measuring electrode].

If platinum measuring electrodes are used during the alkali metal redissolution several anodic current peaks appear (Fig. 2). This is in accordance

with observations made in non-aqueous, organic electrolyte systems [21]. These peaks are clearly due to the formation of lithium-platinum alloys. In contrast to the behaviour in organic solvents, however, peaks are observed even at very positive potentials (compared to the potential of alkali metal deposition). This effect may be due to the high temperature that allows a deeper penetration of lithium into the platinum lattice and consequently a redissolution at more positive potentials. At copper, nickel or titanium measuring electrodes no alloy formation is obtained, which is again in full accordance with the behaviour in non-aqueous solvents [22]. From these results it is clear that copper, nickel, titanium etc. may be used as current collectors for the alkali metal side without problems.

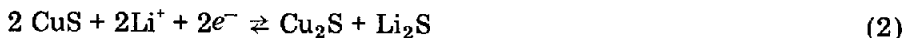
The deposition potential of alkali metals in melts is rather low, about -2.06 V *vs.* Ag/Ag⁺ though the normal potential was determined to be -3.3 V for Li/Li⁺ *vs.* Pt/Pt²⁺ [23]. This marked difference is due to the different potentials of the reference electrodes. This may be easily proven by comparing the potential for Cl⁻/Cl₂ which is $+1.1$ V *vs.* Ag/Ag⁺ and $+0.3$ V *vs.* Pt/Pt²⁺ [23].

The shoulder in the curve of Fig. 2 (which usually appears as a separate peak) is due to the fact that there is only a difference of about 200 mV between lithium and potassium deposition. Regarding cathode materials for cells working with LiCl-KCl eutectic, iron sulphides as well as cuprous and cupric sulphide seem to be promising. To allow comparisons and to estimate the properties and behaviour of lithium/copper sulphide cells, it is important to get some knowledge of the discharge mechanism.

One possible mechanism for the discharge of cupric sulphide is the direct electrochemical reduction and oxidation according to:



On the other hand, a reduction via an intermediate formation of cuprous sulphide has to be taken into account:



In an earlier investigation [13] it was supposed that cupric sulphide is almost entirely converted to cuprous sulphide during the first discharge-charge cycle and that cuprous sulphide is the electrode material during the following cycles. This assertion, however, remains to be proven.

Two observations that might support this assumption are: (i) during charge and discharge of cupric sulphide no potential plateaus are observed (Fig. 3); (ii) according to an energetic calculation made for copper oxides [24] which is based on normal potentials determined by Laitinen and Liu [23] the formation of cuprous oxide is indeed predicted if copper metal and cupric oxide are present together in the eutectic.

However, it does not seem to be correct to apply the normal potentials determined for defined concentrations of dissolved copper(I) and copper(II)

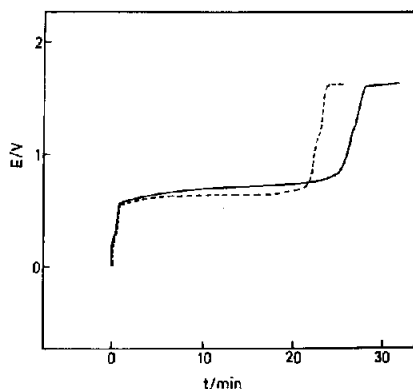


Fig. 3. Galvanostatic reduction curve of a CuS electrode (pressed onto platinum screen) at $i = 50 \text{ mA/cm}^2$; ----, galvanostatic reduction of a CuS-Cu₂S (1:1) mixture electrode at $i = 50 \text{ mA/cm}^2$; ref.: Ag/Ag⁺ in both cases.

species without corrections to cupric and cuprous oxide. Furthermore, it is questionable as to how much one can infer about the behaviour of copper sulphides from the data for copper oxides.

Measurements of the equilibrium potentials of cupric and cuprous sulphide in the eutectic showed that the values are distinctly different from the normal potentials for copper(I) and copper(II) (CuS: $E_R = -200 \text{ mV}$; Cu₂S: $E_R = -180 \text{ mV}$; CuS-Cu (1:1): $E_R = -360 \text{ mV}$; Cu₂S-Cu (1:1): $E_R = -300 \text{ mV}$). These are potential readings from a high impedance voltmeter after equilibration.

From the potential values it is easily understandable that during a galvanostatic discharge curve (Fig. 3) for a cupric-cuprous sulphide (1:1) mixture electrode no potential plateaus are obtained. Even at rather small current densities (about 15 mA/cm^2) no potential steps occur. This behaviour is in marked contrast to observations made in non-aqueous, organic solvents [20, 25]. In this case therefore galvanostatic curves do not provide a suitable basis for assumptions about the discharge mechanism of cupric sulphide.

A more valuable method to test the discharge mechanism of the electrodes is to record c.v. From these measurements it can be shown that cuprous and cupric sulphide indeed exhibit excellent behaviour, allowing oxidation and reduction at reasonably high current densities. A typical c.v. of cuprous sulphide is given in Fig. 4. Furthermore, from these curves information about the discharge mechanism of cupric sulphide is available (Fig. 5).

From Figs. 4 to 7, which are selected as typical examples and from other observations some important conclusions concerning the discharge mechanism may be drawn: (i) potential measurements proved that the equilibrium potentials of cupric and cuprous sulphide and of cupric-cuprous sulphide mixture electrodes are very similar. This conclusion is further supported by galvanostatic discharge curves which exhibit no potential

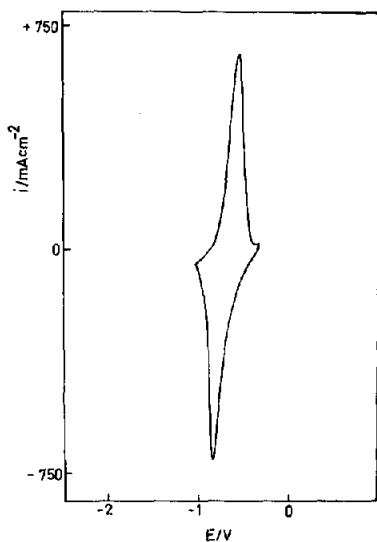


Fig. 4. Cyclic voltammogram of Cu_2S (pressed onto platinum screen). Scan rate: 5 mV/s; counter electrode: platinum-wire; ref.: Ag/Ag^+ .

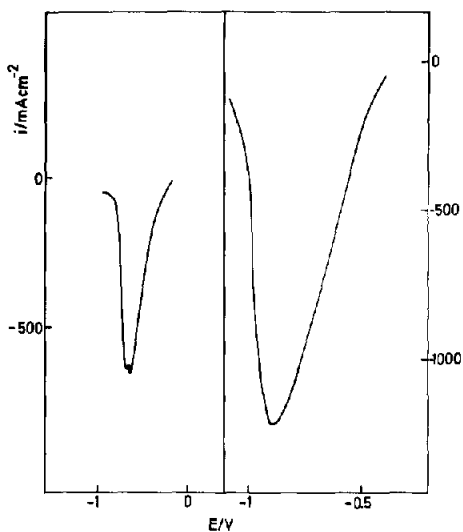


Fig. 5. Reduction peaks of pure CuS (two different experiments); scan rate: 5 mV/s; counter-electrode: graphite; ref.: Ag/Ag^+ .

plateaus; (ii) it may be shown by a chemical experiment that in the presence of a metallic copper/cupric sulphide mixture cuprous sulphide is formed. To prove this, a cupric sulphide/copper (1:1) mixture electrode was exposed to the eutectic without any applied potential. After a few minutes the red colour of the electrode vanished and the electrode was completely black due to the fact that metallic copper was no longer present. If in a control experiment a cuprous sulphide/copper (1:1) electrode is introduced into the melt no colour change occurs; (iii) furthermore cathodic reduction peaks of cupric sulphide in a c.v. are different from that expected for a simple reaction. From Fig. 6, which shows two examples it can be seen that there is a considerable broadening or even splitting of the peaks. This result indicates the presence of at least two electroactive species: cupric and cuprous sulphide (the latter being formed by a chemical reaction between cupric sulphide and copper which is generated during the discharge of cupric sulphide); (iv) the presence of two or more electroactive species is in accordance with the c.v. of a cupric-cuprous sulphide mixture electrode which shows that the first peak (Fig. 6), which may be attributed to the reduction of cupric sulphide, is much smaller than the second peak (reduction of cuprous sulphide) due to the fact that in the chemical reaction between copper and cupric sulphide only about 50% of the initially available cupric sulphide is reduced directly; (v) the curve of a mixture electrode (Fig. 6) further proves that no pure cuprous sulphide is cycled if the starting material was, for example, a cupric-cuprous sulphide (1:1) mixture. On the contrary, a re-formation of the original mixture (or a very similar one) is obtained which is proven by

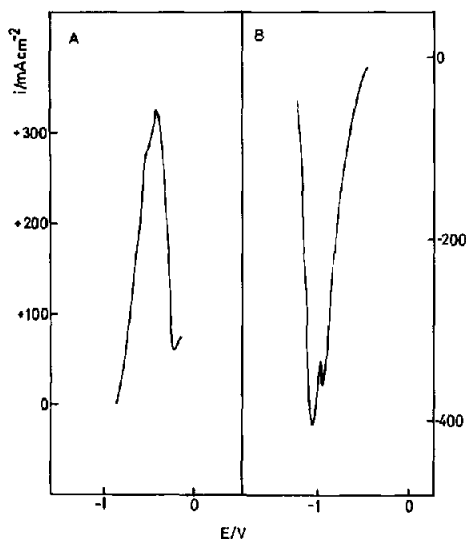


Fig. 6. (A) Oxidation peak of a $\text{CuS-Cu}_2\text{S}$ (1:1) mixture electrode (pressed onto platinum screen); third oxidation cycle of this electrode; (B) reduction peak of this electrode (following curve A); scan rate: 5 mV/s; counter-electrode: platinum; ref.: Ag/Ag^+ .

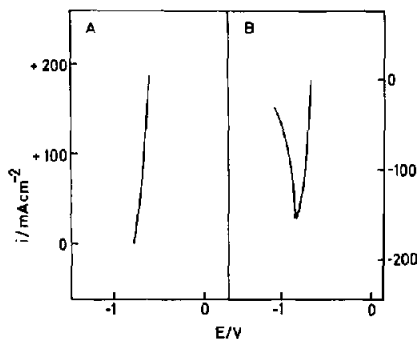


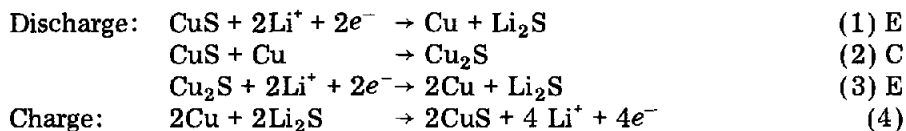
Fig. 7. (A) Partial oxidation of the same electrode as used in Fig. 6; (B) reduction peak of this electrode; sixth oxidation cycle of this electrode. Scan rate: 5 mV/s; counter electrode: platinum; ref.: Ag/Ag^+ .

the fact that during cycling there remain two peaks which are essentially unaffected in their intensity (see *e.g.* Fig. 6 showing the third cycle of a mixture electrode). Furthermore, it can be concluded that the re-oxidation of the mixture also occurs stepwise.

This can be deduced from Fig. 7 where the mixture electrode is not fully oxidized and therefore only one reduction peak is observed; (vi) the behaviour of mixture electrodes and the c.v. of pure cupric sulphide electrodes during cycling additionally suggest a re-formation of cupric sulphide during re-oxidation if this was the starting material. This is also confirmed by (vii); (vii) simple stoichiometric considerations indicate that if cuprous sulphide were to be cycled with cupric sulphide as a starting material part of the lithium (potassium) sulphide would remain unaffected during charge. Because of the potentials of cupric and cuprous sulphide and because of the high solubility of lithium (potassium) sulphide this is quite improbable. Furthermore there would be a considerable difference in the efficiency of the first and the following discharge cycles which is not observed.

From these arguments it cannot be unambiguously proved that the electrochemical discharge of cupric sulphide occurs as a one-step reaction directly with formation of copper though the c.v. suggest this (otherwise a peak corresponding essentially to that of a cupric-cuprous sulphide mixture electrode would be expected). Furthermore, prior results obtained in non-aqueous, organic solvents [20] and also in liquid ammonia [26] support this

assumption. From the points mentioned above it may, however, be concluded that during the discharge of cupric sulphide (and perhaps also during charge) a multiple step reaction due to the chemical formation of cuprous sulphide may occur. The following mechanism for cupric sulphide is suggested:



It cannot be excluded that the charge reaction (4) is somewhat oversimplified and that intermediate stages may occur. If a cupric-cuprous sulphide mixture electrode is used as a starting material, an analogous mechanism for the cupric sulphide portion will apply whereas cuprous sulphide is cycled in a simple way.

The fact that there is only a slight potential difference between cupric and cuprous sulphide during reduction makes it relatively unimportant whether cupric or cuprous sulphide is cycled in a lithium/copper sulphide battery. However, regarding the theoretical energy density of Li/CuS (946 Wh/kg) and Li/Cu₂S (514 Wh/kg) cupric sulphide is, of course, much more favourable and hence the fact that cupric sulphide is re-formed during cycling is very important.

Additional experiments showed that it is not necessary to use copper sulphide as a starting material. A mixture of copper powder and alkali sulphide (in that case sodium sulphide) or even of sulphur works as well as an original sulphide electrode after an anodic formation cycle. As already mentioned the cycling behaviour is extremely good in any case. From galvanostatic discharge curves the extent of utilization was calculated to be about 55 to 60% of the theoretical value for cupric sulphide (based on the reaction: $\text{CuS} + 2e^- + 2\text{Li}^+ \rightarrow \text{Cu} + \text{Li}_2\text{S}$) and it was relatively unaffected by the discharge current density (25 to 50 mA/cm²). It seems to be useful in this context to recall the much smaller extent of utilization in organic solvent electrolytes which is only about 15% in propylene carbonate (even at the very small current density of 0.15 mA/cm² [20]). The much better behaviour of the same materials in the eutectic may be due to the improved diffusion conditions at the elevated temperatures or to a special discharge mechanism that is not known at the moment.

Considering the lithium/copper sulphide system, it is also important to consider all possible side reactions. One possible reaction might be the anodic dissolution of copper with formation of copper chlorides (CuCl and CuCl₂). As shown in Fig. 8, this reaction is observed at a starting potential of about 0 V vs. Ag/Ag⁺ and therefore causes no trouble if enough sulphide is present. The most remarkable effect, however, is that there is only a very small cathodic reaction owing to the reduction of the copper chlorides formed.

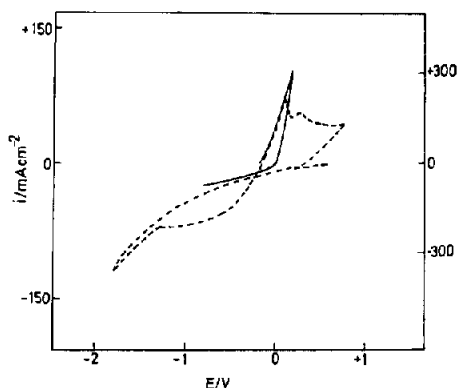


Fig. 8. Oxidation of copper-felt material (no reversible reaction is observed). Scan-rate: 5 mV/s; ----, reduction of dry CuCl_2 (start at cathodic potentials); i -scale at the left-hand side of the Fig.; scan rate: 33.3 mV/s; counter electrode: graphite; ref.: Ag/Ag^+ .

Regarding the results in non-aqueous, organic solvents [27] this behaviour may be attributed to the formation of copper chlorocomplexes (*e.g.* CuCl_2^- , CuCl_4^{2-}) which is favoured by the large excess of chloride ions in the melt. Furthermore, the experimental results (Fig. 6) indicate that there is a rapid diffusion of the complexes into the bulk of the electrolyte because nearly no reduction current is obtained in the c.v. The high solubility of the chlorides may be also proven by introducing CuCl_2 (broken curve in Fig. 6) or CuCl pressed onto platinum screens into the melt. No reduction peak is observed because of the rapid dissolution of the active material. The permanent cathodic background, however, as well as the anodic peak (obviously copper oxidation) indicates that some copper is deposited from the solution containing the dissolved complex species. For the further investigation of the system and possible side reactions, a sulphide electrode (dry sodium sulphide pressed onto a platinum screen) was oxidized in the melt, but though there is a considerable oxidation peak (formation of sulphur) only a very small reduction peak is observed due to sulphur losses by formation of polysulphide species and, at higher temperatures, by vaporization of sulphur ($>445^\circ\text{C}$).

Discussion

The results obtained by c.v. and galvanostatic measurements of CuS , Cu_2S and $\text{CuS-Cu}_2\text{S}$ (1:1) mixture electrodes indicate that the potential difference between cupric and cuprous sulphide during reduction is very small. This, as well as the very high extent of utilization of cupric sulphide during discharge, may be due to special diffusion and temperature conditions in the eutectic. The experimental results proved that lithium (potassium) sulphide has a low solubility in the melt (*e.g.* 0.020 mol/l at 400°C [28]), thus forming an electrode of the second kind with copper sulphide. This is clearly a favourable condition for a secondary battery. However, the long

time properties of the cell will be limited not only by the solubilities of lithium and potassium sulphide but also by that of cupric and cuprous sulphide. The discharge of cupric sulphide seems to produce copper by a direct reduction [20, 26]. If copper metal and cupric sulphide are present together in the eutectic, a chemical formation of cuprous sulphide is obtained. Nevertheless, c.v. measurements indicate that no cycling of cuprous sulphide takes place but, rather that a reformation of the original electrode composition is attained. This is further supported by the potentials and by stoichiometric considerations.

From these results it is clear that in the case of a cupric sulphide starting material there is no simple discharge-charge mechanism but that relatively complicated equilibria exist in which also non-stoichiometric copper sulphide species (such as *e.g.* djurleite and digenite) may also participate. The existence of ternary phases which might be formed during charge and discharge cannot be fully ruled out at the moment. Further work on this subject is in progress and will be published later. The oxidation of copper with the formation of copper chlorides during charge is not a limitation, because the re-formation of copper sulphide is energetically preferred and is obtained at lower potentials.

Although the Li/CuS cell in LiCl-KCl eutectic works very well in principle, there may be serious material problems in building technical cells. For technical purposes especially the testing and introduction of separators seems to be important to minimize self-discharge. The application of an immobilized electrolyte and of immobilized lithium electrodes may be possible ways to solve some of the problems.

Although at the moment, most of the current work is concerned with the Li/FeS₂ cell [14 - 18] because of its high theoretical energy density (1320 Wh/kg), the Li/CuS cell seems also to be a favourable system and relatively high practical energy densities may be available. The fact that only one discharge plateau is observed is an especially favourable condition. Regarding technical applications, the occurrence of two discharge plateaus in the Li/FeS₂ cell is indeed a handicap rather than an advantage especially if it is taken into account that the first plateau is by no means "hard" [14].

Acknowledgement

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References

- 1 R. Jasinski, High Energy Batteries, Plenum Press, New York, 1967.
- 2 J. O. Besenhard and G. Eichinger, J. Electroanalyt. Chem., 68 (1976) 1.
- 3 G. Eichinger and J. O. Besenhard, J. Electroanalyt. Chem., 72 (1976) 1.

- 4 see *e.g.* W. vanGool (ed.), *Fast Ion Transport in Solids*, North-Holland, Amsterdam, 1973.
- 5 R. M. Dell, in M. Kleitz and J. Dupuy (eds.), *Electrode Processes in Solid State Ionics*, Reidel, Dordrecht, Holland, 1976.
- 6 E. J. Cairns and H. Shimotake, *Science*, 164 (1969) 1347.
- 7 *e.g.* P. A. Nelson *et al.*, Report ANL-8039, (1973).
- 8 N. Birk and R. K. Steunenberg, *Adv. Chem. Ser.*, 140 (1975).
- 9 M. J. Weaver and D. Inman, *Electrochim. Acta*, 20 (1975) 929.
- 10 F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, 117 (1970) 904.
- 11 F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, 116 (1969) 607.
- 12 B. Cleaver, A. J. Davis and D. J. Schiffrin, *Electrochim. Acta*, 18 (1973) 747.
- 13 L. A. Heredy, L. R. McCoy, S. Lai and R. C. Saunders, Report N 75-18 741, (1974).
- 14 D. R. Vissers, Z. Tomczuk and R. K. Steunenberg, *J. Electrochem. Soc.*, 121 (1974) 665.
- 15 P. A. Nelson *et al.*, Report N 75-16 990, (1974).
- 16 P. Nelson and D. S. Webster, Report ANL-8064, (1974).
- 17 J. Hall, S. C. Lai, L. McCoy and R. Saunders, Report PB 244 390, (1975).
- 18 K. Abe and T. Ohiku, *J. Electrochem. Soc.*, 122 (1975) 1322.
- 19 Fr. Pat. 1,490,725, (1966).
- 20 G. Eichinger and H. P. Fritz, *Electrochim. Acta*, 20 (1975) 753.
- 21 A. N. Dey, *J. Electrochem. Soc.*, 118 (1971) 1547.
- 22 G. Eichinger, Thesis, Techn. Univ. Munich (1972).
- 23 H. A. Laitinen and C. H. Liu, *J. Am. Chem. Soc.*, 80 (1958) 1015.
- 24 L. H. Thaller, *J. Electrochem. Soc.*, 113 (1966) 309.
- 25 J. P. Gabano, V. Dechenaux, G. Gerbier and J. Jammet, *J. Electrochem. Soc.*, 119 (1972) 459.
- 26 Y. Matsuda, H. Ueyama and Y. Takasu, *J. Electrochem. Soc.*, 123 (1976) 220.
- 27 G. Eichinger and H. P. Fritz, *Z. Naturforsch.*, 28b (1973) 763.
- 28 C. H. Liu, A. J. Zielen and D. M. Gruen, *J. Electrochem. Soc.*, 120 (1973) 67.