

Electrochemical formation of lithium iron(copper)silicide alloys

G. EICHINGER

Institute of Inorganic Chemistry, Technical University of Munich, Lichtenbergstraße 4, D-8046 Garching, West Germany

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The behaviour of copper silicide and of some iron silicides with different silicon contents to lithium deposited electrochemically from organic solvents is investigated. The silicide phases show marked differences. Whereas with copper silicide a time-dependent alloy formation with lithium is observed, the iron silicides exhibit a behaviour ranging from no alloy formation to very rapid alloy formation (depending on the silicon content). The alloyed lithium may be recovered during oxidation with high yields. If some lithium is deposited at the supporting grid of iron silicide electrodes with high silicon content, a rapid surface diffusion with alloy formation is observed.

1. Introduction

Solids exhibiting pure ionic conductivity are of considerable interest for applications as solid electrolytes [1]. Also of increasing interest is the investigation of compounds with mixed conductivity (ionic and electronic) for eventual applications as electrode materials in batteries [2, 3]. In the present investigation the behaviour of some iron silicides and of a copper silicide phase to electrodeposited lithium in some organic solvents is examined.

2. Experimental

The results were obtained using a conventional arrangement for cyclic voltammetry: potentiostat FR 0.5 (G. Bank, Göttingen), voltage scan generator SMP 69 (G. Bank), X-Y recorder HP 7004B. The cell was a double H-type with the anodic compartments separated from the cathodic compartment by glass (D₄) diaphragms. The potential was measured near the surface of the working electrode by means of a Luggin capillary filled with the same electrolyte as used in the cell. An aqueous SCE (Radiometer type K 401) separated from the measuring cell by a diaphragm was used as a reference electrode. The counter electrodes were two pieces of lithium. The solvent dimethylformamide (DMF) used during these experiments was not

especially purified, whereas the propylene carbonate (PC) was dried over molecular sieves (4 Å) and distilled twice.

The silicides were technical products and had the analytical compositions (values supplied by Süddeutsche Kalkstickstoffwerke and Luitpoldhütte) shown in Table 1. The measuring electrodes were prepared by pressing finely ground powders of the alloys onto platinum or nickel screens at a pressure of about 11 000 bar.

3. Results

During this work, the behaviour of iron silicides with variable silicon content to electrodeposited lithium was investigated. Besides these compounds a copper silicide phase with high copper content was tested. In spite of this very high copper content the behaviour of this phase is completely different from that of pure copper. Whereas metallic copper under normal conditions shows virtually no tendency to alloy with lithium, the copper silicide exhibits an alloy formation. This alloy formation may be easily demonstrated by cyclic voltammetry.

In Fig. 1 the behaviour of copper silicide in different solvents is shown. Whereas lithium deposition onto the silicide starts quite near the potential expected for this reaction and there is only a small shoulder (especially marked at slow scan

Table 1. Silicide compositions

| Silicide | (wt%) | | | | | | |
|-----------------|-------|------|------|------|------|------|------------------|
| | Fe | Cu | Si | Al | Ti | Ca | Mg |
| copper silicide | | 88.2 | | | | | |
| iron silicide | 4.63 | | 92.4 | 1.57 | 0.07 | 0.87 | 0.13 traces P, S |
| iron silicide | 23.87 | | 75.1 | 0.97 | 0.06 | | |
| iron silicide | 53.0 | | 45.4 | 2.0 | | | |

rates) before bulk deposition is observed, during the stripping of the lithium two clearly separated oxidation peaks are observed (Fig. 1a). Whereas the peak at more cathodic potentials is due to the reoxidation of unalloyed lithium from the surface, the second peak may be attributed to the reoxidation of alloyed lithium. As shown in Fig. 1b the coulombic efficiency of the second peak increases when the potential is held at the open-circuit potential, whereas the coulombic efficiency of the unalloyed lithium is diminished. There is a relatively good correlation between the two peak areas, thus indicating that lithium from the surface

penetrates into the copper silicide lattice. From this behaviour it may be concluded that a diffusion of lithium into the host lattice is possible but to some extent hindered and that it is a time-dependent reaction.

The effect of time-dependent alloy formation may be demonstrated even more clearly by a galvanostatic reduction and oxidation curve as shown in Fig. 2. In curve A the yield of unalloyed lithium is 56.1% and that of alloyed lithium is 43.5%, whereas in curve B which was recorded with a period of 21 minutes between reduction and oxidation the yield of unalloyed lithium decreases to 33.2% and that of alloyed lithium increases up to 58.6%. The smaller overall yield in experiment B (91.8%) which is nevertheless very high, may be attributed to a reaction of lithium with the solvent.

Furthermore, a galvanostatic deposition of lithium followed by immediate anodic stripping shows that if only low current densities are applied during plating, more alloyed lithium is recovered than if the plating is done at higher current densities (Fig. 3).

The smaller overall yields in Fig. 3 are due to the fact that the solvent was unpurified. Consequently side reactions during lithium plating and stripping play a more important role than in the purified and more stable solvent PC.

The two effects (time dependence and current dependence) indicate that the alloy formation is not very favourable in this case. SEM pictures of copper silicide electrodes after cathodic lithium plating (1 h, 1 mA) show that the whole electrode surface is covered by a film of lithium. This visual observation is confirmed by an X-ray analysis of the surface. By this technique only traces of copper are detected at the surface, thus indicating the formation of a relatively thick and dense film of lithium or reaction products of lithium with the solvent.

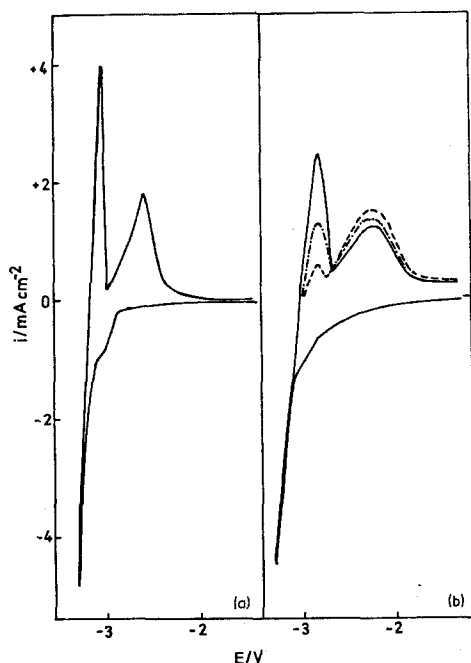


Fig. 1. (a) Cyclic voltammogram of copper silicide (pressed onto platinum screen) in 0.5 M LiClO_4 -DMF (scan rate, 1.66 mV s^{-1}). (b) Cyclic voltammograms of copper silicide in 0.5 M LiClO_4 -PC; first cycle without stop; (- · -) second cycle 2 min stop; (- - -) fourth cycle 6 min stop between reduction and oxidation; the reduction halfcycles coincide, therefore only one cycle is shown (scan rates, 5 mV s^{-1} ; reference electrode, SCE; counter electrodes, lithium).

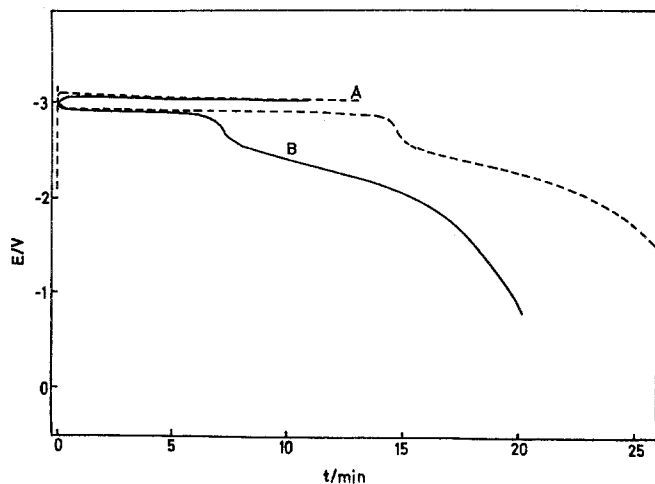


Fig. 2. A. (dashed curve) Galvanostatic deposition and redissolution of lithium at copper silicide (pressed onto nickel screen) in 0.5 M LiClO_4 -PC (current density during deposition, 1 mA cm^{-2} ; during reoxidation, 0.5 mA cm^{-2}). B. Analogous conditions but with a period standing in the solvent (21 min) between deposition and reoxidation of lithium (counter electrodes, lithium; reference electrode, SCE).

An effect of alloying is that lithium is to some extent protected against reactions with the solvent. Whereas lithium deposited from unpurified DMF- LiClO_4 solutions at a copper substrate could not be reoxidized after a few minutes standing in the solvent, lithium deposited under the same conditions onto copper silicide electrodes could be reoxidized to some extent (from the alloy) even after some hours.

The behaviour of the iron silicides is in some contrast to that of the copper silicide. Whereas silicides with high silicon content show a very rapid alloy formation with lithium, the iron

silicides with 45 wt% silicon content show none or only a very slight lithium alloy formation, indicated by a certain dissymmetry of the lithium oxidation peak (Fig. 4).

With compounds containing 75 wt% or about 90 wt% silicon, however, a very rapid alloy formation is observed (Fig. 5).

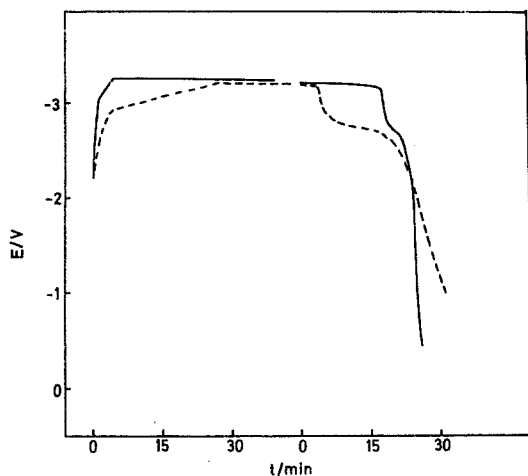


Fig. 3. Galvanostatic deposition and redissolution of lithium at copper silicide (pressed onto nickel screen) in 0.5 M LiClO_4 -DMF; current density, 0.5 mA cm^{-2} . Dashed curve, same electrode; current density, 0.15 mA cm^{-2} . Immediate stripping in every case.

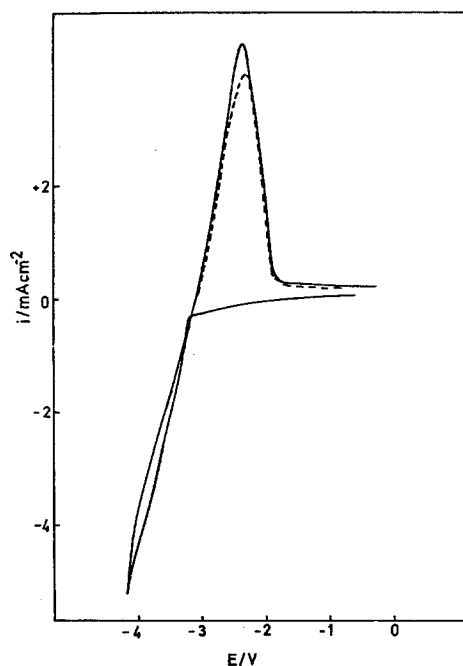


Fig. 4. Cyclic voltammograms of iron silicide (45 wt%) in 0.5 M LiClO_4 -PC (pressed onto nickel screen) (scan rates, 5 mV s^{-1} ; reference electrode, SCE; counter electrodes, lithium). (---) second and third cycle of this electrode.

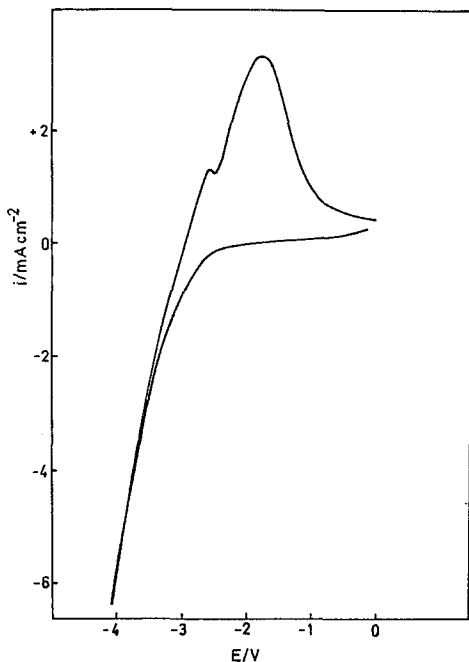


Fig. 5. Cyclic voltammogram of iron silicide (92 wt%) (pressed onto nickel screen) in 0.5 M LiClO_4 -PC (scan rate, 5 mV s^{-1} ; reference electrode, SCE; counter electrodes, lithium).

Cyclic voltammetric as well as galvanostatic curves prove that during the reoxidation of plated lithium no unalloyed, only alloyed, lithium is detected, thus indicating a rapid transport of lithium from the surface into the host lattice and a very fast diffusion in the host lattice. This is confirmed by the observation that during alloy formation or oxidation of the alloyed lithium high current densities can be achieved without serious polarization (more than 15 mA cm^{-2} in organic solvents and 200 mA cm^{-2} in a LiCl-KCl eutectic at about 450°C).

If part of the supporting grid is not covered by the silicide during lithium plating, the metal is of course not only deposited at the iron silicide but also at the grid. During reoxidation a peak corresponding to this unalloyed lithium is observed (Fig. 6a).

If, however, the electrode is allowed to stand in the solvent between plating and stripping, a relatively rapid decrease of the 'free' lithium peak followed by a corresponding increase of the alloyed lithium peak is observed. Fig. 6b shows that within one hour the 'free' lithium plated at

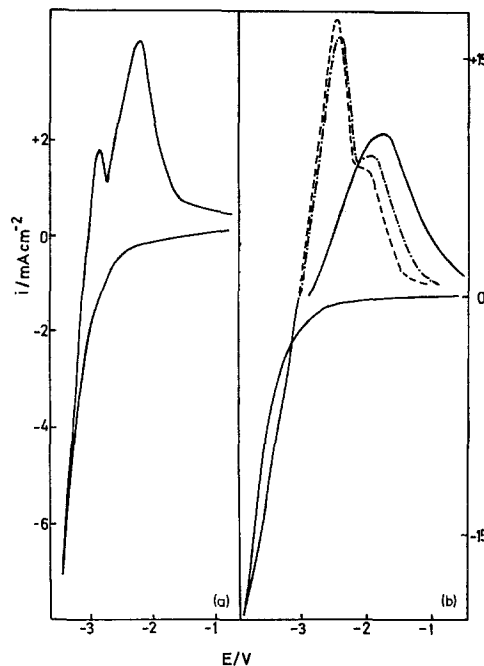


Fig. 6. (a) Cyclic voltammogram of iron silicide (75 wt%) (pressed onto nickel screen) in 0.5 M LiClO_4 -PC; only about one half of the electrode is covered with the silicide. (b) Cyclic voltammograms of the same electrode as in curve (a) at higher current densities; first cycle (—) without stop; second cycle (---) 5 min stop; third cycle (— · —) 55 min stop between cathodic and anodic half-cycle (scan rates, 5 mV s^{-1} ; reference electrode, SCE; counter electrodes, lithium in all cases).

the grid is alloyed. These observations prove that only small amounts of the initially unalloyed lithium reacts chemically with the solvent and that most of this lithium is subsequently alloyed. This behaviour can only be explained by a surface diffusion of the grid-deposited lithium. The relatively rapid and almost quantitative surface diffusion of the deposited unalloyed lithium supports the assumption that the alloy formation with iron silicides with high silicon contents is a very favourable reaction. Small shifts of the anodic peak maximum observed at longer periods of standing in the solvent are probably due to a deeper penetration of alloyed lithium into the host lattice thus requiring more energy for reoxidation.

The different behaviour of copper silicide may be also demonstrated by comparing the SEM pictures with that of iron silicide (75 wt% silicon). In contrast to copper silicide the surface of iron silicide after a lithium plating (16 h, 0.3 mA) is

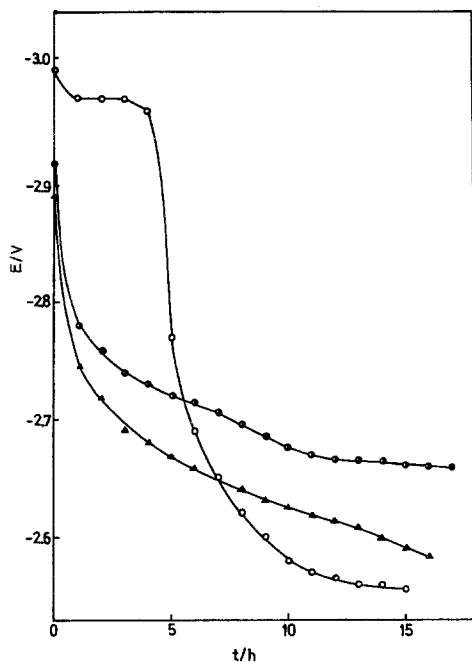


Fig. 7. Open-circuit voltage versus time of silicides in 0.5 M LiClO_4 -PC; copper silicide (○); iron silicide (90 wt%) (●); iron silicide (75 wt%) (▲).

not covered by a lithium film. Only relatively few lithium lumps are to be found at the electrode surface.

The markedly different behaviour of the compounds may be further demonstrated by comparing the open-circuit voltage (OCV) versus time curves of copper silicide and of iron silicides (Fig. 7).

With iron silicides an immediate exponential decay of the OCV is observed, followed by a voltage plateau at a potential corresponding to the lithium-alloyed iron silicide, but with copper silicide the first voltage plateau appears near 3 V versus SCE due to the presence of free lithium. After this lithium is also alloyed or has partly reacted chemically with the solvent so there is also a strong decay in the OCV just as is the case with the iron silicides.

As may be easily shown by an anodic cyclic voltammogram of the solvent PC at smooth platinum electrodes, the reaction products of the unalloyed and also of the alloyed lithium with the solvent are propene and consequently lithium carbonate. It thus proves that the same decomposition reaction of PC is obtained as in the case of some other electrode materials [4]. An additional

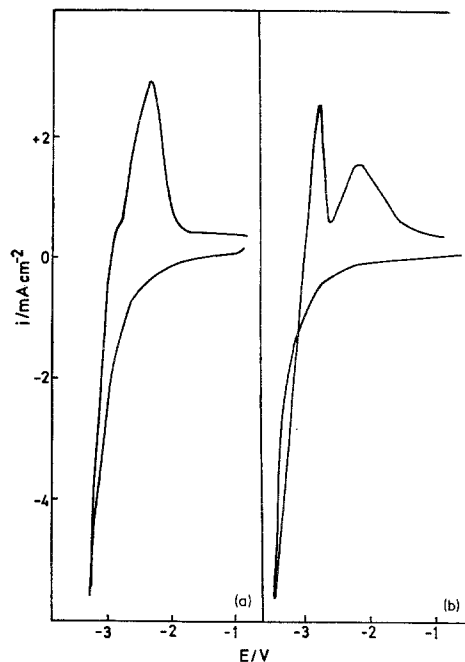


Fig. 8. (a) Cyclic voltammogram of iron silicide (75 wt%) in 0.5 M LiClO_4 -PC; fourth cycle. (b) Same measuring electrode as in (a) after a long period (about 72 h) when the electrode was left in solvent with deposited lithium (scan rates, 5 mV s^{-1} ; reference electrode, SCE; counter electrodes, lithium).

observation confirming these results is given in Fig. 8.

Cyclic voltammograms of iron silicide (electrode without any bare supporting grid) show that no unalloyed lithium may be recovered during anodic stripping. After a long storage time (which leads to decomposition of the alloyed lithium), cyclic voltammograms indicate that some 'free' lithium is deposited at the electrode (Fig. 8). This effect is obviously due to the fact that part of the electrode surface is covered by reaction products (in that case lithium carbonate) thus preventing, to some extent, further alloying.

4. Conclusions

The results obtained during these electrochemical experiments indicate that there are considerable differences in the structures of the silicides tested. Whereas with iron silicides (45 wt% silicon) the diffusion of lithium into the lattice is not favoured, with copper silicide a slow alloy formation is observed. Iron silicides with high silicon contents,

however, exhibit a very rapid alloy formation and thus obviously have open structures allowing rapid movement of lithium in these host lattices. This behaviour is somewhat extraordinary for in most cases, electrochemical alloy formation at room temperature (e.g. with magnesium [5], platinum and other metals [6]) is a slow process (with aluminum being a well-known exception [7, 8]). Except for defined phases, as e.g. FeSi_2 [9], there is little information about the structures of iron silicides. From the phase diagram it seems reasonable to regard these compounds as silicon-enriched FeSi_2 phases [10]. It may be supposed, that with the iron and copper silicides ternary alloys of the type Li_xMeX_y (Me = Fe, Cu; X = Si) are formed. Compounds with defined composition, as e.g. LiCuSi , are known and were prepared from the elements by Schuster *et al.* [11]. Consequently a formation of similar compounds by electrochemical alloying of silicides should be possible.

The results obtained with the different silicides used during this investigation show that there are large differences in the silicide structures strongly influencing the behaviour of the compounds to lithium.

The alloys are only formed with lithium; with sodium (because of its size) no alloy formation is obtained and it may therefore be concluded that only unsolvated lithium is intercalated. The observation that during long periods standing in solvent, alloyed lithium also reacts, may be attributed to diffusional loss, i.e. a reverse diffusion of lithium (from the inner lattice to the surface) due to a concentration gradient in this direction resulting from the chemical reaction

between surface lithium and solvent. Nevertheless, an application of these silicides as electrode materials for lithium anodes in nonaqueous or solid electrolyte cells may be favourable, because of the better storability of alloyed lithium which perhaps may be further improved by film-forming agents inhibiting further reactions between solvent and lithium electrode.

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References

- [1] W. van Gool (editor), 'Fast Ion Transport in Solids', North-Holland, Amsterdam (1973).
- [2] B. C. H. Steele, 'Superionic Conductors' (edited by G. D. Mahan and W. L. Roth) Plenum Press, New York (1976).
- [3] M. S. Whittingham, *J. Electrochem. Soc.* **123** (1976) 315.
- [4] G. Eichinger, *J. Electroanal. Chem.* **74** (1976) 183.
- [5] M. M. Nicholson, *J. Electrochem. Soc.* **121** (1974) 734.
- [6] A. N. Dey, *ibid* **118** (1971) 1547.
- [7] E. C. Gay, D. R. Vissers, F. J. Martino and K. E. Anderson, *ibid* **123** (1976) 1591.
- [8] B. M. L. Rao, R. W. Francis and H. A. Christopher, *ibid* **124** (1977) 1490.
- [9] P. Y. Dusausoy, J. Protas, R. Wandji and B. Roques, *Acta Cryst.* **B27** (1971) 1209.
- [10] M. Hansen and K. Anderko, 'Constitution of Binary Alloys', McGraw-Hill, New York (1958).
- [11] H. U. Schuster and W. Seelentag, *Z. Naturforsch.* **30b** (1975) 804.