Electrodeposition of silicon onto copper substrate from KF-KCl-KI-K₂SiF₆ melt

A V Isakov, A P Apisarov, A O Khudorozhkova, M V Laptev, and Yu P Zaikov

Institute of High-Temperature Electrochemistry of UB RAS, 620137, Russian Federation

Abstract. The electrochemical behavior of Si⁴⁺ deposited onto the Cu substrate, in comparison with one onto C substrate, in the KF-KCl-KI-K₂SiF₆ melt was investigated by the cyclic voltammetry at 993 K. It was found, that the electro reduction of silicon on the Cu substrate proceeds with formation of the Cu-Si alloy (silicon bronze). The electrolysis conditions were determined and the silicon bronze coatings were synthesized by electrolysis in the KF-KCl-KI-K₂SiF₆ melt. The surface of deposits was examined by the electron microscopy with EDS analysis. The deposits contained only copper and silicon. The microhardness of the coatings achieved 1618 HV. The microhardness of the obtained films was tested in air during one month: it decreased from 1618 to 380 HV.

1. Introduction

The silicon coatings and silicon-based materials provide new feasibilities for increasing the efficiency of the chemical power sources [1]. A promising process for obtaining the silicon nanomaterials is electroreduction in molten salts [2-5]. The silicon deposits with various morphology and structure, from the thin films-coatings to nanomaterials in the form of fibers, can be obtained by electrolysis of the KF-KCl-K₂SiF₆-based melts [5]. The silicon nanomaterials as a component of the negative electrodes in the lithium-ion batteries (LIB) allow increasing their lithium capacity and expanding the temperature operation range. The main degradation mechanism of the silicon anodes in the LIB is destruction under the influence of the lithium intercalation-deintercalation as a result of a change in volume [6]. Due to the size effect, the silicon nanomaterials have a better ability to withstand the destruction. The likely direction of improving the structure of the anode material in the LIB is the obtaining the thin-film materials, in which the interacting component is located inside the metal matrix can be films of the silicides of the copper-silicon bronzes can be considered as perspective materials. In most cases, copper is used as a current lead in the LIB. It has a high electrical conductivity and satisfactory mechanical processing, however it has a rather low abrasion and oxidation resistance. There are several ways to increase an efficiency of using the copper-based materials. The first is to apply the alloys (bronzes). The second way is to create the copper-based composites. In order to improve the operating characteristics, the surface hardening by the diffusion saturation with one or more chemical elements can be performed.

The properties of the silicon bronzes have been studied mainly in the range of the silicon content in copper up to 7.5 wt% [7, 8]. This is due to the fact that the casting silicon bronzes alloys have such a concentration. The effect of the silicon concentration (from 2.5 to 7.5 wt%) on the mechanical properties of the silicon bronze in the temperature range of 200-400 °C was studied in [7]. It was revealed that the strength and hardness values of such silicon bronzes corresponded to the properties
of the Cu (80%) - Sn (20%) alloys, but the toughness even exceeded them. The hardness of the 92.5% Cu-7.5% Si composition decreased from 200 HV to 180 HV in the range of 200-400 °C. It was recognized that the Cu (80%)-Sn (20%) and 92.5% Cu-Si (7.5%) alloys had a similar crystalline structure. The microhardness increased from 125 to 200 HV with increasing the silicon content in the bronze, at 200 °C. It was found in [9] that the increase in the strength of the silicon bronzes is basically connected with the appearance of a significant amount of the silicon intremetalides and a change in the shape and size of this phase.

When preparing the anodic assemblies of a complex shape for the Li-ion batteries, it is necessary to take into account the deformation of materials. A study regarding the deformation of the silicon bronzes with the composition of Cu-Si (5%) was performed by the authors [10]. It was determined that the silicon-copper alloys were a unique object, in which the destruction energy of the crystalline lattice is very low, that resulted in the effect of a twinning during the deformation. It was found [10] that, by choosing the conditions, it was possible to obtain a decrease in the threshold voltage and an increase in the limit deformation. Such a change in properties, if it can be extrapolated to alloys with a higher silicon concentration, will be useful for application in the current sources.

In [11], the measured microhardness of the Cu-Si alloy (3 wt. %) under normal conditions was 180 HV, the addition of 0.8 wt% tungsten allowed to increase this magnitude to 358 HV. It was revealed that the change in microhardness was accompanied by a change in the size, shape of the grains, and resulted in an increase in the electrical conductivity of the alloys by 14.9% compared to the original alloy. The thermoelectric dependences of these materials have also been investigated [12, 13] in the silicon content range up to 3%. The obtained values are acceptable for the formation of a full-value anode material for the Li-ion batteries.

However, it should be considered that the capacity of the silicon-copper film will depend directly on the silicon content. With an increase in the silicon content, the lithium capacity will increase. At the same time, when obtaining materials, the conditions should be created when the saturation of one component with another has a minimum of obstacles in the form of the high coefficients of the mutual diffusion during the alloy formation. The mechanisms of the silicon diffusion in copper have been studied in [14, 15] and the kinetic parameters of the processes have been determined. It was established that the volume diffusion coefficient of Cu as a function of temperature can be described by the equation $D=3.0\cdot10^{-4}\exp\left(-0.18eV/kT\right)$ [15]. It is equal to $3\cdot10^{-5}\text{ cm}^2\cdot\text{s}^{-1}$ at 600 °C. Similar order of magnitude has the diffusion coefficient of the complex anions in molten salts in the same temperature range. Accordingly, the electrolytic silicon saturation of copper and vice versa should not have the significant diffusion difficulties associated with the diffusion from the electrode / electrolyte boundary in the electrode body. The interaction of the thin films of silicon and copper at temperatures of 300, 600, and 900 K was studied by molecular dynamics in [16]. It was found that the diffusion processes begin to predominate in the vicinity of the Si / Cu interface as the temperature increased, and the alloy was formed and compacted near the surface. With rising temperature, the fraction of the face centered cubic (FCC) structure increases, but the internal compressive stresses inside the Cu-Si film decrease. It should be noted that we have not found any work related to the study of the mechanical properties of the silicon-copper alloys thin films on any substrates. However, the principal possibility of using the silicon-copper films formed by the laser sintering method in the Li-ion CCS has been demonstrated in [17].

It is known that the diffusion coatings with the controlled distribution of elements in the surface layer can be obtained in molten salts [18, 19]. The technological processes are characterized by a relatively simplicity and low cost. However, the synthesis of the silicon-copper films in molten salt has not been studied yet. There is no information regarding the mechanism of the cathodic silicon reduction on a copper substrate in the promising KF-KCl-KI-K2SiF6 melt.
2. Experimental

2.1. Preparation of salts

The electrochemical reduction of silicon was carried out in the KF-KCl-KI-K$_2$SiF$_6$ melts, which were prepared from the individual chemicals: the KCl and KF·HF (99.9 wt. %) supplied by Uralkali, the K$_2$SiF$_6$ (99 wt. %) and KI (99 wt. %) supplied by Vekton.

The potassium chloride was dried in a glassy carbon crucible under vacuum at $T = 923$ K for 4 hours. The salt was then melted and kept at 1073 K for an hour, after which it was cooled.

The potassium hexafluorosilicate was purified from the oxygen impurities by treating with the ammonium fluoride. The K$_2$SiF$_6$ was mixed with 2 wt. % NH$_4$F and sustained at 673 K for 6 hours in a glassy carbon crucible. The gaseous HF, released during the thermal decomposition of the ammonium fluoride, reacted with the oxide impurities contained in the K$_2$SiF$_6$ with formation of the gaseous compounds of silicon, ammonia, and water vapour in accordance with the reaction (1).

$$4\text{NH}_4\text{F} + \text{SiO}_2 = 4\text{NH}_3\uparrow + \text{SiF}_4\uparrow + 2\text{H}_2\text{O}\uparrow$$

The potassium iodide was additionally iodinated using the crystalline iodine in order to remove the oxygen-containing impurities. A mixture of iodine and potassium iodide was placed in a glass-carbon container with a closed lid and an iodization process was carried out at 773 K until the evaporation of iodine under the given conditions. The reaction can be written as:

$$2\text{K}_2\text{O} + 2\text{I}_2 = 4\text{KI} + \text{O}_2$$

2.2. Electrochemical cell

The experiments were performed in a three-electrode sealed water-cooled stainless steel cell in an atmosphere of the high-purity argon at 993 K (Figure 1). The container for the melt was a glass-carbon crucible. To prevent the interaction of the melt-sublimation products with the cell walls, the electrolyte container was placed in a nickel vessel. To prevent the disturbance of the inertness of the atmosphere above the melt, when adding the potassium iodide to the melt and changing the electrodes, a sluice device was provided. Electron grade silicon was used as an auxiliary electrode and a reference electrode.

![Figure 1. Scheme of cell for voltammetric investigation: 1 - retort; 2 - graphite heel; 3 - nickel protection vessel; 4 - cooling jacket; 5 - rubber seals; 6 - quasi-reference electrode; 7 - working electrode; 8 - sluice; 9 - auxiliary electrode; 10 - gas tubes; 11 - glassy carbon crucible; 12 - melt;](image-url)
The working electrode was glass-calcium plates 40 × 5 × 2 mm (SU-2000, 99.999 wt. % purity, Uralmetallgraphite) and copper plates of the same size (99.999 wt. %, UMMC). The typical geometric area of the working electrode varied from 1.6 to 2.1 cm².

The electrolyte was prepared from the individual fluoride, chloride, and iodide and potassium hexafluorosilicate by the following procedure. First, a mixture of KF and KCl was placed in a glass-carbon container, heated to 373 K, sustained for 2 hours, then heated to a temperature of 573 K and sustained for an hour. Then, the mixture was heated to 1023 K, held for an hour and poured into a graphite mold. The KF-KCl electrolyte was stored in a desiccator.

The electrolyte of the required composition was prepared directly in an electrochemical cell using the KF-KCl and the individual KI and K₂SiF₆ electrolytes.

Prior to conducting the electrochemical studies, the purification electrolysis was carried out in two steps. The first one is potentiometric electrolysis with an insoluble graphite anode, having a surface area of the order of 4 cm². The criterion for the end of the potentiostatic purification was the decrease of the anode current density to below 1 mA/cm². This required about 2-3 hours of electrolysis. The second step is galvanostatic electrolysis with a graphite cathode. The cathode current density was 20 mA·cm⁻². The electrolysis time is 2 hours. The final criterion for the success of the purification was the absence of a peak on the curve when the potential was swept to the anode side at 1.2 V relative to the silicon quasi-reference electrode.

2.3. Experimental techniques

The electroreduction study was performed by cyclic voltammetry. The registration of voltammograms and electrolysis were carried out with the help of the potentiostat-galvanostat AUTOLAB 302N. The sweep rate interval was from 0.1 to 1.5 V·s⁻¹. The resistance of the electrolyte was determined by the impedance method and was automatically compensated during the potentiodynamic tests.

The obtained solid silicon deposits were washed with a solution of hydrochloric acid. The metallography was carried out by scanning electron microscopy with the installation of micro-X-ray spectral analysis (EDS) on a JMS-5900LV instrument.

The impurities determination in the deposits, electrolyte, and original salts was conducted by the atomic-emission method with inductively coupled plasma on the iCAP6300 Duo (Thermo Scientificinc.). The Vickers hardness tests were performed using Durascan (Emcotest).

3. Results and discussion

The investigation of the cathode process was carried out using cyclic voltammetry in the molten KCl-KF(1:2)–KI(75 mol.%)–K₂SiF₆(0.26 mol.% Si). The typical data is presented in Figure 2.

![Figure 2. Typical cyclic voltammetry curves obtained in molten KCl-KF (1:2)-KI (75 mol.%) - K₂SiF₆ (0.26 mol.% Si) at 993 K (Cu substrate, scan rate 0.1-0.5 V·s⁻¹).](image-url)
The $E$-$i$ dependences (figure 2) indicate the presence on the copper substrate of the cathode process associated with the electrodeposition of new phase, and the corresponding anode process. The current change from 0 to 0.55 V is explicated by the electroxidation of new phase released during the anode process.

The section of the enhanced cathode current (from 0.2 to 0 V) presents on the cyclic voltammograms at all sweep rates. In the indicated section, the current takes negative values and is connected with the electroreduction of the substance. This section is located at more positive potentials than the potential the Si reference electrode (set to 0V). This indicates that there are conditions for the Si-Cu alloy formation during the cathode process on the copper substrate in the molten KCl-KF (1:2) –KI (75 mol. %) - $K_2SiF_6$ (0.26 mol. % Si).

The peak bifurcation takes place in the cathode area at increasing the sweep rate from 0.1 to 0.5V/s. Two signals (cathode peaks) appear during the cathode process, which are associated with two different reactions. The current increase during the first process $c_1$ (figure 2) is likely connected with the formation of the Si-Cu alloy. Whereas the second cathode peak $c_2$ is likely related to the crystallization reaction of the elementary silicon on the substrate surface. The peak bifurcation at the high sweep rates can be explained by the increasing diffusion difficulties at the Cu/Si interface. In the cathode process, these difficulties are more significant at the high sweep rates whereas at the anode dissolution they are expressed at the low sweep rates (waves $a_1$ and $a_2$). We assumed that the $a_1$ process is related to the silicon dissolution from the surface, and the process $a_3$ is associated with the silicon dissolution from the Cu-Si alloy.

At the present, there are no available techniques for the analysis of the cyclic voltammetric diagrams obtained on the interacting substrates. In order to investigate the silicon electrodeposition processes on the copper substrate it was necessary experimentally to separate these processes by stages.

The separation of the two processes were carried out by the registration of the cyclic voltammetry curves obtained on the glassy-carbon and copper substrates in the KCl-KF (1:2)-KI (75 mol. %) $K_2SiF_6$ (0.26 mol. %) melt (figure 3).

![Figure 3. Cyclic voltammetric curves obtained in the KCl – KF (1:2) – KI (75 mol. %) - $K_2SiF_6$ (0.6 mol. % Si) vs the Si reference electrode at 0.1 V·s$^{-1}$: a – for Cu and Glassy carbon substrates; b – Dependence of $E_{al}$ from scan rate.](image)

The peak registered in the cathode area (figure 3) is related to the Si electroreduction process and the corresponding peak of dissolution is in the anode area. Within the framework of this study, a number of electrons participating in the reaction can be calculated according to the following reaction:
\[ E_{p/2k} - E_{pk} = 2.20 \frac{RT}{nF} \]  

where \( E_{pk} \) is the peak potential, V; \( E_{p/2k} \) is the semipeak potential, V; \( R \) is the universal gas constant, 8.3145 m\(^3\)·kg·s\(^{-2}\)·K\(^{-1}\)·mol\(^{-1}\); \( T \) is the process temperature, K; \( F \) is the Faraday constant, (96485 KJ·mol\(^{-1}\)); \( n \) is the number of electrons participating in the reaction;

The number of electrons participating in the reaction was 3.98 ± 0.2 for the potential sweep rate range 0.01-0.08 V/s. Thus, one of the reaction of the cathode process is the silicon electroreduction:

\[ Si^{4+} + 4e = Si^{0} \]   

The behavior of the voltammetric dependences (Figure 2 and 3) indicates that the process of the currentless transfer is possible in the system. In this case, the transfer of electronegative silicon to the Si-Cu alloy, where the Si activity is less than 1, is the current formation process. This can be proved by the decreasing the surface area of the cathode process on 20% (for example, Fig.3). The partial Gibbs energy change for the given process will be connected with the emf of the currentless circuit [19]:

\[ \Delta G_{Si} = -nFE = RT \ln a_{Si} \]   

where \( \Delta G_{Si} \) is the change of the Gibbs energy of the Cu-Si alloy formation, J/mol; \( E \) is the emf of the circuit connected with the B alloy formation \( a_{Si} \) is the activity of Si in the alloy with copper.

In these conditions in both cases (for the glassy carbon and copper electrodes) the reversible dynamic concentration equilibrium is created. The equilibrium is revealed in the behavior of the voltammetric dependences. By the deduction of the potential values in the peak beginning (point 1) (Figure 3) from the values of the silicon cathode deposition, related to the alloy formation (point2), it was possible to exclude \( \Delta E_{e} \), connected with the electrochemical reaction, and to detect \( \Delta E_{a} \), associated with the alloy formation. The \( E_{a1} \) dependence on the potential sweep rate is presented in figure 2a. It was established that the \( E_{a1} \) value remains constant at investigated rates of the sweep potential in the range of a measurement error. This means that the alloy formation process is reversible in these conditions. The fraction of the energy in the process brought by the alloy formation stage remains constant. This is also verified by the fact that the contribution to the current of the cathode process from the alloy formation and from the electrochemical reaction is separated to the full extent. The silicon limiting concentration in the film can be calculated from this diagram at the certain process temperature. This allows estimating the \( \Delta G_{Si} \) by the equation (4). For the given conditions, \( \Delta G_{Si} \) was -88.766 KJ/mol. This energy is less than \( \Delta G_{Si} \) - 101.1 KJ/mol, calculated in [20] for 993 K for the interaction of the individual substances (Si and Cu). However, both values are comparable to each other.

The electrolytic deposits on the copper substrate were obtained by electrolysis in the KCl-KF (1:2) – KI (75 mol.%) - \( K_{2}SiF_{6} \) (0.26 mol.%) melt. The conditions and chemical composition of the obtained deposits are presented in table 1.

The homogenous diffusion coatings of silver containing Si were obtained in the galvanostatic mode. It was found that the Si concentration rises with increasing the electrolysis duration.

The electron microscopy data and the distribution maps of the elements in the obtained deposits are shown in figure 4.
Table 1. Conditions of the silicon electrodeposition.

| No. | Melt composition | Cathode current density, A·cm⁻² | U, V | Time of deposition, s | Alloy composition, wt% | Microhardness, HV | Deposits After deposition | Deposits After 1 month |
|-----|------------------|---------------------------------|------|------------------------|------------------------|---------------------|--------------------------|--------------------------|
| 1   | KCl-KF (1:2)-KI (75 mol. %)-K₂SiF₆ (0.26 mol. %) | 0.1 | 0.2 | 2 | Si 7.20 | Cu 67.17 | 44.2 | - | - |
| 2   | KCl-KF (1:2)-KI (75 mol. %)-K₂SiF₆ (0.26 mol. %) | 0.2 | 0.2 | 300 | Si 18.53 | Cu 67.92 | 44.2 | 350 | 150 |
| 3   | K₂SiF₆ (0.26 mol. %) | 0.25 | 0.25 | 900 | Si 23.99 | Cu 76.01 | 44.2 | 1618 | 380 |

Figure 4. SEM and EDS data of deposits obtained by electrolysis in the KCl-KF(1:2)-KI (75 mol. %)-K₂SiF₆ (0.26 mol. %) melts: a’, b’, c’ – silicon distribution; a”, b”, c” – cooper distribution.
It was determined that together with the Si crystallization and its diffusion into the alloy the accumulation of the Si clusters on the electrode surface takes place with increasing the electrolysis time. However, during the long time electrolysis (Figure 4, c) the silicon almost completely diffuses throw the electrode surface and forms the alloy. The rest of the Si spreads homogeneously along the surface of the Si-Cu alloy. The data analysis of the electrodeposition and chemical composition of coating allows composing the alloy formation stage as aim for the reaction:

$$3\text{Cu} + \text{Si} = \text{Cu}_3\text{Si} \quad (6)$$

Thus, the overall reaction occurring on the electrode can be written as:

$$n\text{Cu} + \text{Si}^{4+} + 4\text{e} = \text{Cu}_3\text{Si} \quad (7)$$

where $n$ is the molar fraction of the copper atoms in the surface layer of the copper electrode;

The samples obtained during long time electrolysis, were subjected to microhardness measurements according to the Vickers technique in order to estimate the influence of the Si addition onto the substrate. The value for the sample (table 1, No. 3) 1618 HV can be considered as enormously high, the same is valid to 358 HV (table 1, No. 2). Moreover, the deposits had a grey color with metallic glitter. After suspending in air during 1 month, the samples changed their color to cupreous. The microhardness of the samples decreased. For example, for the sample No. 3 (table 1) it changed from 1618 to 380HV. However, this level is still quite high and can be juxtaposed with the tungsten 0.8% content in the Cu-Si alloy (3 wt. %) [11]. The degradation mechanism of the properties of the obtained films will be studied more detailed.

Thus, it was established that the films obtainment occurs throw two parallel processes (4) and (6). The obtained films have quite high Si content, but the substrate bending did not lead to the films flaking. This is a positive factor for the preparation of electrodes with the large surface area for the lithium-ion batteries.

4. Conclusions

The electrochemical behavior of the Si$^{4+}$ in the KF-KCl-KI-K$_2$SiF$_6$ melt was investigated by cyclic voltammetry technique substrate in comparison with one onto C substrate at 993 K onto Cu. It was found that the silicon electroreduction on the copper substrate proceeds with the formation of the Cu-Si alloy (silicon bronze).

The mechanism of the cathode process for the Si-Cu films obtainment was established. (7). It was revealed that two processes occur during obtaining two layers of Si-Cu: the Si eletcrocrystallization (4) and the alloy formation (6). It was found that the changes in the conditions of the reaction behavior (4) do not affect the alloy formation process (6). The Gibbs energy change of the alloy formation process for the sweep rate range from 0.1 to 0.5 V·s$^{-1}$ was stable (~88.766 KJ·mol$^{-1}$).

It was recognized that the Cu-Si alloy’ films with the Si content up to 23.99 wt. % can be obtained by electrolysis in the KF-KCl-KI-K$_2$SiF$_6$. The decrease in the microhardness of the obtained films at keeping in open air during one month from 1618 to 380HV was detected.

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5. References

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