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Silicon electrodeposition from the KF–KCl–K_2SiF_6 and KF–KCl–KI–K_2SiF_6 melts

S.I. Zhuk[1,2], **L.M. Minchenko**[1], **A.V. Suzdaltsev**[1,2], **A.V. Isakov**[1], **Yu.P. Zaikov**[1,2]

[1] **Institute of High-Temperature Electrochemistry of Ural Branch of the Russian Academy of Sciences**
20 Akademicheskaya str., Ekaterinburg, 620137, Russia

[2] **Ural Federal University n.a. the First President of Russia B.N. Eltsin**
19 Mira str., Ekaterinburg, 620002, Russia

✉ Andrey V. Suzdaltsev (suzdaltsev_av@ihte.uran.ru, a.v.suzdaltsev@urfu.ru)

Abstract: Silicon and silicon-based materials find extensive applications in metallurgy, microelectronics, and other emerging industries. The field of use of synthesized silicon varies based on its morphology and purity. This study employs voltammetry, galvanostatic electrolysis, and scanning electron microscopy to examine the impact of KI surfactant (in mol.%) to 66.5KF–33.3KCl–0.23K_2SiF_6 melt at 750 °C on the electrowinning kinetics of silicon ions and the morphology of silicon deposits formed on a glassy carbon electrode. The findings demonstrate that the addition of potassium iodide to the KF–KCl–K_2SiF_6 melt at a concentration of 2 mol.% induces changes in interfacial tension at the boundary between the glassy carbon, melt, and atmosphere. Consequently, the wetting of the glassy carbon with the melt decreases, leading to a reduction in the actual working surface area and, consequently, a decrease in cathode current while maintaining current density. Taking into account this effect and employing an algebraic estimation of the influence of the melt meniscus shape, it is postulated that the addition of KI does not significantly affect the kinetics of the cathode process. Nevertheless, the impact of KI addition on the morphology of electrodeposited silicon is mentioned. During the electrolysis of the KF–KCl–K_2SiF_6 melt, fibrous silicon deposits with arbitrary shapes are formed on the glassy carbon electrode, whereas the addition of 2 and 4 mol.% of potassium iodide to the melt leads to the agglomeration and smoothing of silicon deposits under the same electrolysis conditions (cathode current density: 0.02 A/cm^2, electrolysis duration: 2 h). The obtained results indicate the potential to manipulate the morphology of electrodeposited silicon for specific applications in various fields..

Keywords: silicon, voltammetry, electrodeposition, morphology, KF–KCl melt.

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Электроосаждение кремния из расплавов KF–KCl–K_2SiF_6 и KF–KCl–KI–K_2SiF_6

С.И. Жук[1,2], **Л.М. Минченко**[1], **А.В. Суздальцев**[1,2], **А.В. Исаков**[1], **Ю.П. Зайков**[1,2]

[1] **Институт высокотемпературной электрохимии УрО РАН**
620137, Россия, г. Екатеринбург, ул. Академическая, 20

[2] **Уральский федеральный университет им. первого Президента России Б.Н. Ельцина**
620002, Россия, г. Екатеринбург, ул. Мира, 19

✉ Андрей Викторович Суздальцев (suzdaltsev_av@ihte.uran.ru, a.v.suzdaltsev@urfu.ru)

Аннотация: Кремний и материалы на его основе широко используются в металлургии, микроэлектронике и других развивающихся отраслях промышленности. Области применения синтезируемого кремния зависят от его морфологии и чистоты.

В данной работе методами вольтамперометрии, гальваностатического электролиза и сканирующей электронной микроскопии изучено влияние поверхностно-активной добавки KI в расплав (мол.%) 66,5KF–33,3KCl–0,23K_2SiF_6 при температуре 750 °С на кинетику электровосстановления ионов кремния и морфологию получаемых на стеклоуглеродном катоде кремниевых осадков. Показано, что введение в расплав KF–KCl–K_2SiF_6 йодида калия в количестве 2 мол.% приводит к изменению межфазного натяжения на границе стеклоуглерод–расплав–атмосфера, а именно к снижению смачиваемости стеклоуглерода расплавом, в результате чего реальная рабочая поверхность, а соответственно, и катодный ток уменьшаются при сохранении плотности тока. С учетом подобного воздействия и алгебраической оценки влияния формы мениска расплава сделано предположение, что добавка KI практически не сказывается на кинетике катодного процесса. При этом отмечено заметное влияние добавок KI на морфологию электроосаждаемого кремния. При электролизе расплава KF–KCl–K_2SiF_6 на стеклоуглероде формируются волокнистые осадки кремния произвольной формы, в то время как добавление 2 и 4 мол.% йодида калия в расплав приводит к агломерации и сглаживанию осадков кремния при прочих равных условиях электролиза (катодная плотность тока – 0,02 А/см^2, время электролиза – 2 ч). Полученные результаты указывают на возможность регулирования морфологии электроосаждаемого кремния с целью дальнейшего его применения в той или иной сфере.

Ключевые слова: кремний, вольтамперометрия, электроосаждение, морфология, расплав KF–KCl.

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Introduction

In contemporary industry, silicon and silicon-based materials hold substantial significance. Silicon finds extensive application in the manufacturing of alloys comprised of ferrous and non-ferrous metals, functional powdered materials, photoelectric converters, and electronics [1—3]. The considerable lithium capacity of silicon enables the utilization of composite materials derived from it as anode materials in lithium-ion power sources [4].

Silicon with specific properties and morphologies such as solid deposits, nano- and micro-sized wires, fibers, and tubes can be obtained through the electrochemical deposition of silicon from molten salts and ionic liquids [5—14]. Electrochemical techniques are well studied for production and refinement of various materials in molten salts [15—20]. In this context, herewith, it is feasible to regulate the electrodeposition process by adjusting factors such as cathode current density, cathode overvoltage, process temperature, and melt composition [21—23].

The commonly used electrolytes in laboratory settings for silicon production are water-soluble KF—KCl based melts [8—12]. These electrolytes facilitate electrolysis within a temperature range of 650—750 °C. Currently, the kinetics of the cathode process has been extensively investigated in relation to temperature, concentration of silicon-containing electroactive ions, substrate material, and polarization conditions. Experimental batches of silicon deposits were obtained under various electrolysis parameters, and a diagram was proposed to illustrate the impact of these parameters on the morphology of silicon deposits [12]. In the examined melt with K_2SiF_6 concentrations up to 5 wt.% on graphite, it is possible to produce solid, porous, and well-developed silicon deposits in the form of fibers with arbitrary shapes and ordered submicron particles. The formation of a solid deposit is favored by a low cathode current density, while an increase in current density results in a deposit with higher specific area. This phenomenon can be attributed to several factors:

— an excess growth rate of existing nuclei compared to the growth rate of new nuclei;

— silicon primarily deposition on the surface of nuclei due to diffusion limitations concerning the supply of electroactive ions to the cathode surface;

— co-deposition of potassium and its intercalations into graphite.

The likelihood of potassium co-deposition is supported by the observation that solid silicon deposits were formed on a silver cathode at elevated cathode current densities [12]. This further validates the previously mentioned ability to manipulate the morphology of deposited silicon during the electrolysis of molten salts by modifying the process parameters.

Furthermore, the morphology of silicon deposits can be regulated by incorporating additives that affect the physicochemical properties of the electrolyte. Particularly, this pertains to modifications in the electrical conductivity and surface tension of the molten medium. As such, in previous studies [24—26], the use of molten electrolytes based on iodides (KF—KCl—KI—K_2SiF_6, NaI—KI—K_2SiF_6) has been proposed for silicon electrodeposition. However, it should be noted that the iodide concentrations in these systems are 75 mol.% and higher, which complicates the comprehensive understanding of iodide's influence on both the kinetics and mechanisms of silicon recovery from electroactive ions, as well as the resulting deposit morphology during electrolysis.

The present work focuses on investigating the impact of KI on the kinetics of the cathode process on glass carbon in a KF—KCl melt, as well as the morphology of deposits formed during electrolysis.

Experimental

The measurements and electrodeposition tests were conducted using salts of chemical purity grade (Vekton, Russia), which were subjected to precleaning procedures. The salts were purified by hydrofluorination (KF, K_2SiF_6) [9], iodination (KI) [20], and preliminary potentiostatic cleaning electrolysis in molten salts [27]. The electrochemical measurements and silicon electrodeposition were performed under an argon atmosphere using a sealed stainless-steel retort (Fig. 1), which was placed inside a vertical resistance furnace. The electrolyte was contained in a glassy carbon crucible within a graphite beaker. In order to maintain the argon atmosphere upon the addition of KI to the melt, the cell design was equipped with a gateway. A glassy carbon electrode served as the working electrode, while monocrystalline silicon was utilized as a reference quasi-electrode and auxiliary electrode. Tungsten rods were used as current leads for the electrodes. The melt temperature was set and controlled at 750±2 °C using Pt/Pt—Rh thermocouples and a TP703 thermoregulator (Varta, Russia).

Current voltage dependencies were recorded using a glassy carbon electrode immersed in a melt consisting of 66.5KF—33.3KCl—0.23K_2SiF_6 (mol.%) at a temperature of 750 °C. The measurements were conducted using an AutoLab 302N potentiostat—galvanostat (Metrohm, Netherlands). In order to assess the impact of KI on wetting behavior of the glassy carbon electrode with the KF—KCl—K_2SiF_6 melt, the experiments were performed with a partially immersed electrode. The depth of immersion was varied from 5 to 15 mm. Electrolysis of the 66.5KF—33.3KCl—0.23K_2SiF_6 (mol.%) melt, with the addition of 2 and 4 mol.% KI, was carried out under the same condition of cathode current density (0.02 A/cm^2) and glassy carbon cathode immersion (15 mm).

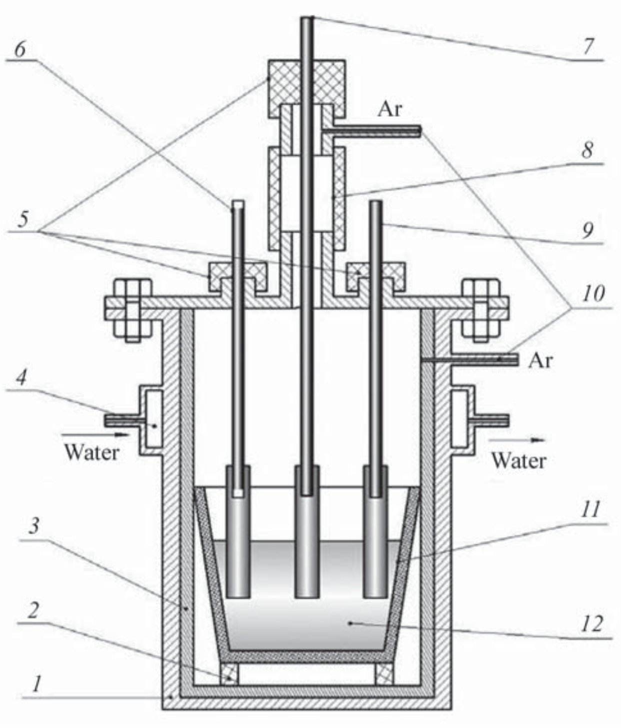

Fig. 1. Schematic view of experimental cell

1 – stainless-steel retort; ***2*** – graphite stand; ***3*** – nickel screen; ***4*** – cooling shell; ***5*** – rubber seals; ***6*** – quasi-reference electrode; ***7*** – working electrode; ***8*** – gateway; ***9*** – auxiliary electrode; ***10*** – inlet/outlet channels of inert gas; ***11*** – glassy carbon crucible; ***12*** – melt

Рис. 1. Схема экспериментальной ячейки

1 – реторта из нержавеющей стали; ***2*** – графитовая подставка; ***3*** – никелевый стакан; ***4*** – кожух охлаждения; ***5*** – уплотнения из вакуумной резины; ***6*** – электрод сравнения; ***7*** – рабочий электрод; ***8*** – шлюз; ***9*** – вспомогательный электрод; ***10*** – каналы подвода/отвода инертного газа; ***11*** – стеклоуглеродный тигель; ***12*** – расплав

The concentration of silicon in the melt before and after electrolysis was determined through atomic emission spectroscopy with inductively coupled plasma, employing an iCAP 6300 Duo Spectrometer (Thermo Scientific, USA). The morphology of the silicon deposits was examined utilizing a JMS-5900LV scanning electron microscope (JEOL, Great Britain), while the phase composition was assessed using a Rigaku D/MAX-2200VL/PC diffractometer (Rigaku, Japan).

Results and discussion

Electrochemical measurements. Figure 2 illustrates the current voltage dependencies acquired at a glassy carbon cathode immersed in a KF—KCl—K_2SiF_6 melt at a temperature of 750 °C, both with and without the addition of 2 mol.% KI.

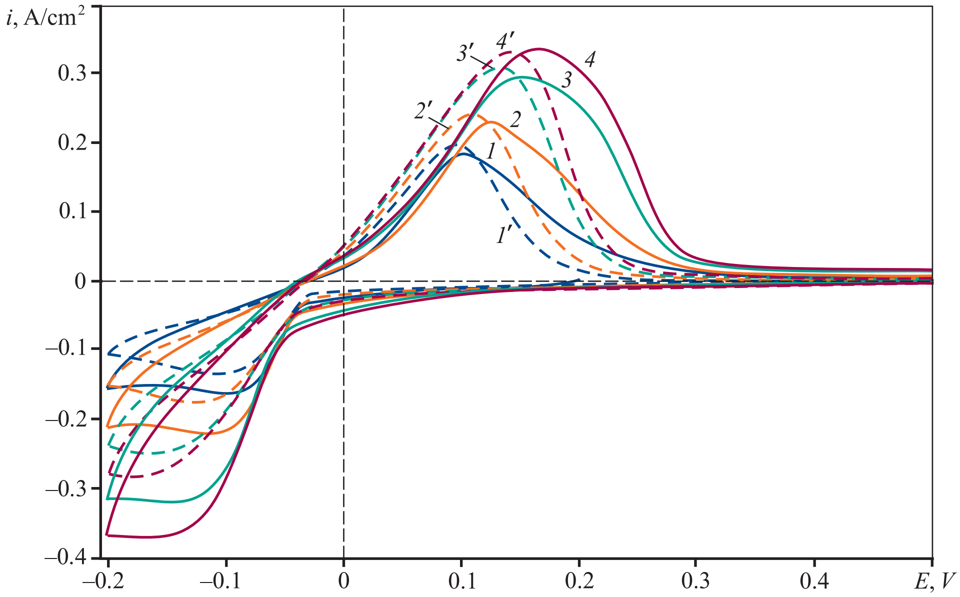

Fig. 2. Current voltage dependencies obtained on glassy carbon at 750 °C in 66.5KF–33.3KCl–0.23K_2SiF_6 (***1–4***) and 65.2KF–32.6KCl–2.0KI–0.23K_2SiF_6 (***1′–4′***) melts (mol.%)
Potential scanning rate, V/s: ***1***, ***1′*** – 0.1; ***2***, ***2′*** – 0.2; ***3***, ***3′*** – 0.4; ***4***, ***4′*** – 0.7

Рис. 2. Вольт-амперные зависимости, полученные на стеклоуглероде при температуре 750 °C в расплавах (мол.%) 66,5KF–33,3KCl–0,23K_2SiF_6 (***1–4***) и 65,2KF–32,6KCl–2,0KI–0,23K_2SiF_6 (***1′–4′***)
Скорость развертки потенциала, В/с: ***1***, ***1′*** – 0,1; ***2***, ***2′*** – 0,2; ***3***, ***3′*** – 0,4; ***4***, ***4′*** – 0,7

The dependencies display a distinct cathode peak and an anode peak, indicating the electroreduction of silicon ions and the oxidation of electrodeposited silicon, respectively. The presence of a single cathode peak suggests that the cathodic process occurs in a single stage: $Si^{4+} + 4e^- = Si^0$. The non-symmetry of the anode peak suggests a two-stage oxidation of silicon, involving the oxidation of silicon to various electroactive ions and the sluggish diffusion of silicon-containing ions within the electrode vicinity. As the scanning rate increases, the peak potential of the cathode current density shifts towards the negative region. This behavior is typical for electrochemical reactions following a mechanism of quasi-reversible or irreversible electrochemical processes. Furthermore, at potentials more negative than –0.2 V, a distinct wave is observed, indicating the initiation of electroreduction of potassium cations.

Similar trends were observed in the KF—KCl—K_2SiF_6 melt with the addition of 2 mol.% KI, indicating that the underlying mechanism of the process remains unchanged. However, some differences were observed in the current-voltage dependencies obtained with the addition of KI. These differences include lower cathode currents and narrower anode peaks, indicating alterations in the kinetics of anodic dissolution of silicon. The reduction in cathode current can be attributed to a change in the wetting angle between the glassy carbon electrode and the melt upon the addition of potassium iodide. This change is likely caused by modifications in the interfacial tension

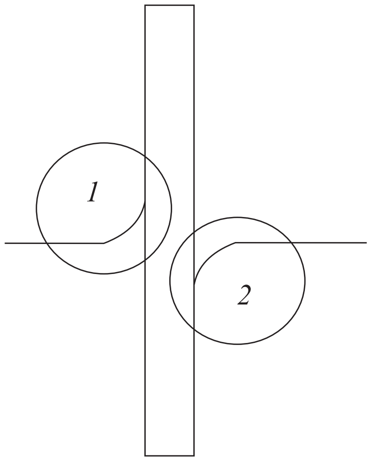

Fig. 3. Changes in meniscus shape upon KI addition to KF–KCl–K_2SiF_6 melt
1 – w/o KI; ***2*** – 2 mol.% KI

Рис. 3. Схематическое отображение изменения формы мениска при добавлении KI в расплав KF–KCl–K_2SiF_6
1 – без KI; ***2*** – 2 мол.% KI

at the boundary between the glass carbon electrode and the KF—KCl—K_2SiF_6 melt due to the presence of KI. It should be noted that the influence of KI may primarily affect the surface of the working glass carbon electrode rather than directly affecting the cathode current. This effect is illustrated schematically in Fig. 3.

Analysis of KI influence. In order to consider the impact of the meniscus formed during polarization on the three-phase boundary between the electrode, melt, and atmosphere, current-voltage dependencies were obtained with varying immersions of the working electrode into the melt. The goal was to account for the actual surface area of electrode-electrolyte contact affected by the presence of the melt meniscus. The measurement error associated with the true electrode surface area was estimated based on the cathode peak currents using the following equations:

$$I_1/(S_1 + \Delta S) = I_2/(S_2 + \Delta S) = I_3/(S_3 + \Delta S), \quad (1)$$

$$\Delta S = (I_1S_2 - I_2S_1)/(I_2 - I_1) =$$
$$= (I_1S_3 - I_3S_1)/(I_3 - I_1) = (I_2S_3 - I_3S_2)/(I_3 - I_2), \quad (2)$$

where I_1, I_2, I_3 represent the currents of the cathode peak corresponding to electrode submersions of 5, 10 and 15 mm, respectively, A; S_1, S_2, S_3 denote the measured working surface areas of the electrode at the same submersions, cm^2; ΔS represents the measurement error of the true electrode surface area caused by the occurrence of the melt meniscus at the three-phase boundary, cm^2.

Figure 4 depicts the current density of the cathode peaks as a function of the potential scanning rates for different submersions of the glass carbon electrode. When the electrode is submerged to a depth of 5 mm in the KF—KCl—K_2SiF_6 melt without KI, the peak of the cathode current density, taking into account the measurement error ΔS, is at its maximum. However, the peak decreases as the depth of electrode submersion increases. Conversely, in the presence of 2 mol.% KI, the trend is reversed. This suggests that the addition of KI leads to a decrease in the wetting angle of the glassy carbon electrode, as illustrated in Fig. 3.

The analysis based on Equations (1) and (2) indicates relative changes in the true surface area of the working electrode due to the formation of a melt meniscus during polarization. For the KF—KCl—K_2SiF_6 melt the estimated relative change is +12.9 %, while for the same melt with the addition of 2 mol.% KI, the relative change is –10.9 %. These calculations were performed under equivalent conditions. Considering the wetting phenomena, the actual peaks of cathode current density in the KF—KCl—K_2SiF_6 melt with and without 2 mol.% KI differ by 9 % (as shown in Fig. 4), which falls within the range of measurement error. Therefore, based on the voltammetry measurements, it can be concluded that the addition of 2 mol.% KI does not significantly affect the rate of silicon electrodeposition. However, it is worth noting that KI may exert a more noticeable influence on the formation of silicon nuclei, which, in turn, can impact the morphology of the deposited material.

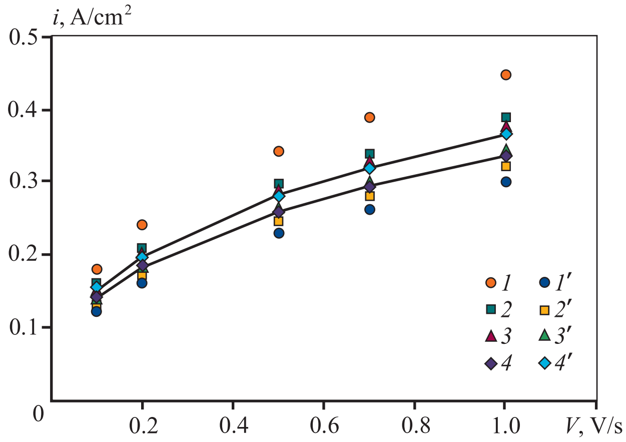

Fig. 4. Current density of cathode peaks as a function of potential scanning rate with various immersions (***1***, ***1′*** – 5 mm; ***2***, ***2′*** – 10 mm; ***3***, ***3′*** – 15 mm; ***4***, ***4′*** – calculated with accounting for ΔS) of glassy carbon in KF–KCl–K_2SiF_6 melt with addition of 2 mol.% KI (***1′***–***4′***) and without it (***1***–***4***)

Рис. 4. Зависимости плотности тока катодных пиков от скорости развертки потенциала при разных погружениях (***1***, ***1′*** – 5 мм; ***2***, ***2′*** – 10 мм; ***3***, ***3′*** – 15 мм; ***4***, ***4′*** – рассчитанные с учетом ΔS) стеклоуглеродного электрода в расплаве KF–KCl–K_2SiF_6 с добавкой 2 мол.% KI (***1′***–***4′***) и без нее (***1***–***4***)

Electrodeposition of silicon from KF—KCl—KI—K_2SiF_6 melts. The effect of iodide addition on the morphology of silicon deposits during electrodeposition from KF—KCl—K_2SiF_6 melt was investigated. The experiments were conducted using melts without KI, as well as with the addition of 2 and 4 mol.% KI. The electrolysis was performed at a temperature of 750 °C, using galvanostatic mode with glassy carbon plates prepared in a similar manner as the cathodes. The cathode current density was set at 0.02 A/cm^2, and the electrolysis duration was 120 minutes.

Figure 5 presents SEM-images of the obtained silicon deposits. In the melt without KI, the deposits appear as

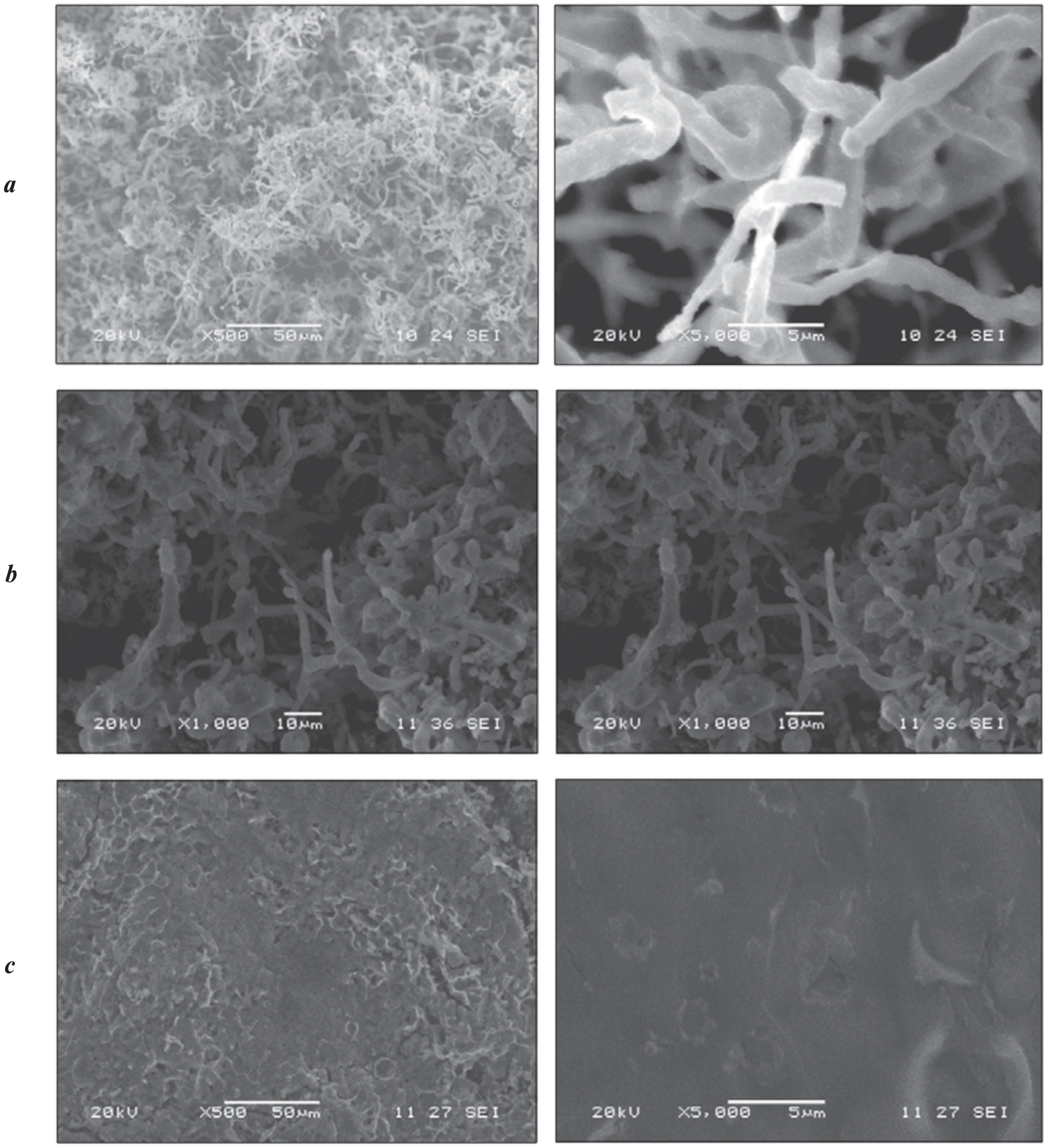

Fig. 5. SEM-images of silicon deposits obtained upon electrolysis of KF–KCl–K_2SiF_6 melt on glassy carbon at cathode current density of 0.02 A/cm^2 and at 750 °C

KI content, mol. %: ***a*** – 0; ***b*** – 2; ***c*** – 4

Рис. 5. Микрофотографии осадков кремния, полученных при электролизе расплава KF–KCl–K_2SiF_6 на стеклоуглероде при катодной плотности тока 0,02 А/см^2 и температуре 750 °С

Содержание KI, мол.%: ***a*** – 0; ***b*** – 2; ***c*** – 4

fibers with arbitrary shapes, having an average diameter of 1—2 µm. Upon adding potassium iodide in amounts of 2 and 4 mol.% to the melt, the silicon fibers agglomerate, resulting in the formation of solid silicon deposits. Energy dispersion analysis of the deposits revealed the presence of silicon and oxygen, with the oxygen content reaching up to 5 wt.% in terms of silicon dioxide. *X*-ray phase analysis of the deposits yielded similar results (see Fig. 6).

The findings from the electrochemical measurements and experiments on silicon electrodeposition highlight the significant influence of iodide on the morphology of silicon deposits. Specifically, with the addition and increased concentration of iodide in the melt, a smoothing

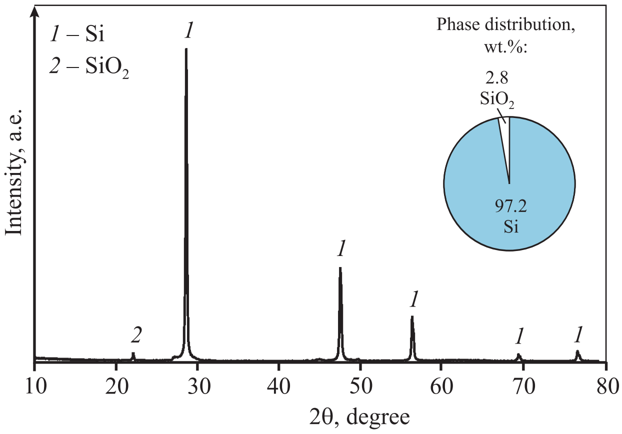

Fig. 6. Diffraction pattern of typical silicon deposit obtained upon electrolysis of KF–KCl–K_2SiF_6 melt with KI addition

Рис. 6. Дифрактограмма типичного осадка кремния, полученного при электролизе расплава KF–KCl–K_2SiF_6 с добавкой KI

effect on the deposit can be expected, assuming all other conditions remain constant.

Conclusions

The influence of potassium iodide (KI) as a surfactant on the kinetics of electroreduction of silicon ions and the morphology of silicon deposits on a glassy carbon cathode was studied using voltammetry, galvanostatic electrolysis, and scanning electron microscopy. The research was conducted in a 66.5KF—33.3KCl—0.23K_2SiF_6 melt (mol.%) at a temperature of 750 °C.

The results demonstrated that the addition of 2 mol.% KI to the KF—KCl—K_2SiF_6 melt alters the interfacial tension at the boundary between the glassy carbon electrode, melt, and environment. This leads to a decrease in the wetting of the glassy carbon electrode by the melt, resulting in a reduction in the actual working surface area and cathode current while maintaining current density. By accounting for this impact and estimating the influence of the melt meniscus shape, it was concluded that the addition of KI does not significantly affect the kinetics of the cathode process. During the electrolysis of the KF—KCl—K_2SiF_6 melt, fibrous silicon deposits with arbitrary shapes are formed on the glass carbon cathode. However, the addition of 2 and 4 mol.% KI to the melt causes the silicon deposits to agglomerate and become smoother under equivalent electrolysis conditions (cathode current density: 0.02 A/cm^2, electrolysis duration: 2 hours.

These findings indicate the possibility of adjusting the morphology of electrodeposited silicon, which can be advantageous for specific applications in various fields.

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Information about the authors

Sergey I. Zhuk – Junior Researcher of the Laboratory of Electrode Processes, Institute of High-Temperature Electrochemistry of Ural Branch of the Russian Academy of Sciences (IHTE UB RAS); Junior Researcher of the Laboratory of Electrochemical Devices and Materials, Ural Federal University n.a. the First President of Russia B.N. Eltsin (UrFU).
https://orcid.org/0000-0003-2889-7318
E-mail: ZhukSI83@mail.ru

Lyudmila M. Minchenko – Cand. Sci. (Chem.), Engineer of the Laboratory of Electrode Processes, IHTE UB RAS.
https://orcid.org/0000-0001-6067-5251
E-mail: l.minchenko@ihte.uran.ru

Andrey V. Suzdaltsev – Dr. Sci. (Chem.), Leading Researcher of the Laboratory of Electrode Processes, IHTE UB RAS; Head of the Laboratory of Electrochemical Devices and Materials, UrFU.
https://orcid.org/0000-0003-3004-7611
E-mail: suzdaltsev_av@ihte.uran.ru, a.v.suzdaltsev@urfu.ru

Информация об авторах

Сергей Иванович Жук – мл. науч. сотрудник лаборатории электродных процессов Института высокотемпературной электрохимии Уральского отделения Российской академии наук (ИВТЭ УрО РАН); мл. науч. сотрудник научной лаборатории электрохимических устройств и материалов Уральского федерального университета им. первого Президента России Б.Н. Ельцина (УрФУ).
https://orcid.org/0000-0003-2889-7318
E-mail: ZhukSI83@mail.ru

Людмила Михайловна Минченко – к.х.н., инженер лаборатории электродных процессов ИВТЭ УрО РАН.
https://orcid.org/0000-0001-6067-5251
E-mail: l.minchenko@ihte.uran.ru

Андрей Викторович Суздальцев – д.х.н., вед. науч. сотрудник лаборатории электродных процессов ИВТЭ УрО РАН; заведующий научной лабораторией электрохимических устройств и материалов УрФУ.
https://orcid.org/0000-0003-3004-7611
E-mail: suzdaltsev_av@ihte.uran.ru, a.v.suzdaltsev@urfu.ru

Andrey V. Isakov – Cand. Sci. (Chem.), Head of the Laboratory of Electrocrystallization and High-Temperature Electroplating, IHTE UB RAS.
https://orcid.org/0000-0002-0192-3048
E-mail: ihte_uran@mail.ru

Yuriy P. Zaikov – Dr. Sci. (Chem.), Prof., Scientific Supervisor of the IHTE UB RAS; Head of the Department of Technology of Electrochemical Production, UrFU.
https://orcid.org/0000-0001-6138-3955
E-mail: zaikov@ihte.uran.ru

Андрей Владимирович Исаков – к.х.н., заведующий лабораторией электрокристаллизации и высокотемпературной гальванотехники ИВТЭ УрО РАН.
https://orcid.org/0000-0002-0192-3048
E-mail: ihte_uran@mail.ru

Юрий Павлович Зайков – д.х.н., проф., научный руководитель ИВТЭ УрО РАН; заведующий кафедрой технологии электрохимических производств УрФУ.
https://orcid.org/0000-0001-6138-3955
E-mail: zaikov@ihte.uran.ru

Contribution of the authors

S.I. Zhuk – preparation of electrolytes, electrochemical measurements, electrodeposition, registration of the research results, participation in the writing of the article.

L.M. Minchenko – installation manufacturing, microscopic analysis, electrodeposition.

A.V. Suzdaltsev – definition the purpose of the work, writing the text of the article.

A.V. Isakov – discussion of the research results.

Yu.P. Zaikov – general management of research.

Вклад авторов

С.И. Жук – приготовление электролитов, электрохимические измерения, электроосаждение, оформление результатов исследований, участие в написании статьи.

Л.М. Минченко – изготовление установки, микроскопический анализ, электроосаждение.

А.В. Суздальцев – постановка цели работы, написание текста статьи.

А.В. Исаков – обсуждение результатов исследований.

Ю.П. Зайков – общее руководство исследованиями.

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