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Rationalisation and optimisation of solid state electro-reduction of SiO_2 to Si in molten $CaCl_2$ in accordance with dynamic three-phase interlines based voltammetry

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ABSTRACT

The cyclic voltammograms of a silica sheathed tungsten disc (W-SiO_2) electrode in molten $CaCl_2$ at 900 °C exhibited an unusually increasing reduction current with decreasing the potential scan rate. When the cathodic limit was less negative than −1.00 V (vs. a quartz sealed Ag/AgCl reference electrode), the reduction current was also smaller in the forward (negative) potential scan than that in the reversed (positive) scan. However, at a given reduction charge, the reduction current increased with the scan rate, following approximately a logarithm law. These unique features have been elaborated according to the dynamic model of the conductor (silicon)/insulator (silica)/electrolyte (molten salt) three-phase interlines (3PIs). Combining the voltammetric observations with the composition analysis of the products from potentiostatic electrolysis of porous silica pellets, the optimal potential window was identified to be from −0.65 V to −0.95 V. In this potential range, silica was converted to pure silicon with the oxygen content being less than 0.5 wt.%. At potentials more negative than −0.95 V, the reduction of Ca^{2+} ions in the reduction-generated porous silicon layer led to the formation of various calcium silicides. These findings can help the development of an electrolytic process for clean, efficient and inexpensive production of high purity silicon.

1. Introduction

The present industrial extraction of silicon is through the carbothermic reduction of SiO_2 at 1700 °C or higher temperatures [1,2], resulting in large energy consumption [~13 kWh (kg-Si)$^{-1}$, counting only the electricity for heating], low energy efficiency (<30%), and serious carbon emission (mass ratio of CO_2:Si > 3). In addition, large stretches of forests are being destroyed to satisfy the huge demand of hard charcoal in the industrial production chain. In response to the growing demand for sustainable development, it is urgent to search for improved alterative processes without compromising the product quality and quantity. Recently, following the FFC Cambridge Process that was first demonstrated for titanium extraction from solid TiO_2, [3] direct electro-reduction of solid SiO_2 to silicon in molten $CaCl_2$ has been confirmed in different laboratories [4–24]. This novel electrochemical process has a number of predicted merits, including (1) mild process conditions, (2) lower energy consumption, (3) less or zero carbon emission, (4) fewer contaminants (C, P, Fe, etc.), and potentially (5) direct production of solar-grade silicon [18,19].

As it has been suggested [5,15,16,20], direct electro-reduction of insulating silica starts at the initial current collector/solid SiO_2/molten $CaCl_2$ three-phase interlines (3PIs). The reduction-generated Si, which has a reasonably electronic conductivity, is porous due to the decrease in molar volume from SiO_2 to Si. Simultaneously, molten $CaCl_2$ enters the pores, leading to the formation of new Si/SiO_2/$CaCl_2$ 3PIs which propagate along the surface of, and also penetrate into the solid SiO_2 until complete reduction. When SiO_2 is reduced, the O^{2-} ions move into the neighbouring electrolyte in the reduction-generated porous silicon layer, and are then transported to the bulk electrolyte and finally discharge at the anode.

It has been shown that the 3PI propagation along the surface is much faster than that in the depth direction of solid SiO_2 [5]. When the reduction occurs on the surface of solid SiO_2, the influence of diffusion of the O^{2-} ions is negligible and the reduction rate is mainly determined by charge transfer. A thin layer 3PI model has been proposed to assist the understanding of the propagation of surface 3PIs [9]. However, in the depth direction, the reduction could be affected by O^{2-} ion diffusion and also ohmic polarization,

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both electronic and ionic, in the reduction-generated porous silicon layer. Accordingly, a penetration 3PI model has been developed [15,16], which also helps the determination of some kinetic parameters of the reduction process, including ρ (total resistivity) and D_R (diffusion coefficient). The penetration 3PI model has been experimentally verified for the electro-reduction of solid SiO_2 to Si in molten $CaCl_2$ [15].

Nevertheless, the understanding achieved so far has not yet been applied to cyclic voltammetry of solid SiO_2 in molten $CaCl_2$. Such a work would otherwise help identify, for example, the optimal cathode potentials for controlling both process rate and product quality, which however requires the proper design of an effective working electrode. The pinpoint electrode on a quartz plate [4] and the metallic cavity electrode [21] with metal oxide powders have been engaged in voltammetric studies. Whilst these two designs have enabled important insights of the electro-reduction in general, considering the fact that SiO_2 is an insulator, it is desirable to introduce well defined initial metal/SiO_2 contacts with minimised metal/electrolyte interface. In another design [5], a thin tungsten (W) wire was sealed in a quartz tube on a gas flame. The end face of the W-wire was turned into a silica surrounded small W-disc by grinding. The structure of this W-SiO_2 electrode is similar to that of a conventional disc electrode. However, instead of using the metal disc as the working interface to enable charge transfer to or from electro-active species in a liquid electrolyte, the W-SiO_2 electrode employs the intimately contacted W/SiO_2/$CaCl_2$ 3PI as the initial charge transfer location.

Following previous brief descriptions [5,9,10], we report here in greater depth the dynamic 3PIs based voltammetric behaviour of the W-SiO_2 electrode in molten $CaCl_2$ at 900 °C, aiming to further understand the electro-reduction of SiO_2 to Si in solid state as well as to find an optimized electrolysis potential window for the production of pure silicon. The reduction mechanism has been derived from cyclic voltammetric and chronoamperometric results based on the 3PI models.

2. Experimental

The quartz sheathed tungsten disc (W-SiO_2) working electrode (280 μm in diameter) was made as described before [5,10,15] for voltammetry and chronoamperometry. Fig. 1a shows an optical scanning image of the W-SiO_2 electrode. After cathodic polarisation, as revealed by Fig. 1b and c, the W-disc was surrounded by a ring of brown product whose width (W) could be directly measured. The measured width of the brown product ring and the charge passed during the potentiostatic reduction are plotted in Fig. 1d. Section 3.2.5 presents more discussion.

Anhydrous $CaCl_2$ (~96% purity, Shanghai Silian Chemicals) was used to prepare the molten salt bath following procedures described elsewhere, during which, the moisture in the salt was carefully removed both thermally and electrochemically [21–23]. A graphite crucible served as the molten salt container and also counter electrode (anode). Pre-electrolysis of the molten salt was carried out at a cell voltage of 2.5 V between the graphite anode and a nickel sheet cathode for about 12 h to minimise moisture and other impurities in the molten salt. The use of nickel as the cathode was to alloy with, and hence remove most of the Mg^{2+} impurity (about 0.3 wt.%) in the as-received anhydrous $CaCl_2$ [15]. After prolonged pre-electrolysis with the Ni cathode, the molten $CaCl_2$ prepared from the anhydrous $CaCl_2$ could be significantly cleared of Mg^{2+} impurity and exhibit an electrochemical property comparable with that prepared from the ASC grade $CaCl_2{\cdot}2H_2O$ (containing 0.005 wt.% Mg^{2+}, Amresco, Inc.). Therefore, the much cheaper anhydrous $CaCl_2$, which would be preferable for industrial applications, was primarily engaged in this study.

Cyclic voltammograms (CVs) and chronoamperometric plots were recorded using a computer controlled CHI660A Electrochemical System (Shanghai Chenhua, China). All electrochemical experiments were carried out at 900 °C using the quartz sealed high temperature reference electrode composed of a Ag wire in the inner electrolyte of 10% AgCl + 45% NaCl + 45% KCl (in mole percentage). As reported previously [10], this reference electrode exhibited a very stable potential of *ca.* 1.3 V against the reduction potential of Ca^{2+} to Ca in $CaCl_2$, determined by the content of AgCl in the inner electrolyte, and also by the Donnan potential resulting from different activities of some cations, e.g. Ca^{2+} and Na^+, on the two sides of the semi-permeable quartz membrane [10,25]. In this paper, unless specified otherwise, all potential data are reported with reference to this reference electrode. Table 1 lists the electrode potentials of different reactions. Particularly, it can be seen that the potential difference between the reduction of SiO_2 to Si and that of Ca^{2+} to Ca as calculated from thermodynamic data (0.838 V) compares very well with that measured experimentally (0.83 V) in this work. This agreement was the basis for the choice of the quartz sealed Ag/AgCl reference electrode and the molten salt in this work.

Potentiostatic electrolysis (or chronoamperometry) of cylindrical porous silica pellets was carried out to obtain enough product at designated potentials for further analysis. The pellets were made by pressing (4 MPa) the SiO_2 powder (99% purity, 10 μm in average particle size) and sintering in air at about 900 °C for 2 h (16 mm in diameter, 3.3 mm in thickness, about 1.0 g in mass and 35% in porosity). An assembled cathode was fabricated by sandwiching the pellet between two molybdenum wire meshes. The potentiostatic electrolysis lasted usually for 10 h for comparison purposes. The electrolysed pellet was cooled under argon. Prudent observations were paid to the reaction between the electrolysis product and water (especially for bubble evolution) and its influence on the properties of the products. Then, the product was washed in 0.l M HCl and dried in vacuum at 80 °C. After electrolysis at −0.55, −0.60 and −0.65 V, there was a white solid core in the pellet, suggesting incomplete reduction in the given 10 h. This unreduced core was removed before the pellet went through further analysis.

The Uniscan C800 colour optical scanner (Tsinghua Unisplendor Co. Ltd., China) and the Hitachi x-650 scanning electron microscope (SEM) were used for microscopic analysis. Elemental composition of the electrolysis products were obtained by energy dispersive X-ray analysis (EDX) (Genesis 7000, EDAX, Mahwah, NJ, USA). Since the lower detection limit of EDX was about 0.5 wt.%, the respective elements were regarded to be absent in the product if the detection was less than 0.5 wt.%. For the same reason, oxygen analysis results from EDX are presented in this paper for qualitative discussion only, but more accurate results were obtained from the LECO RO-416DR inert gas fusion oxygen analyser.

3. Results and discussion

3.1. CVs of a W-wire electrode

The cyclic voltammogram (CV) of a bare tungsten (W) wire electrode (280 μm in diameter, *ca.* 1.5 cm in immersion depth, and *ca.* 13 mm^2 in electrode/molten salt interfacial area) was first recorded in the molten $CaCl_2$. As shown in Fig. 2a, metal-deposition-like currents (C1) on the W-wire are clearly seen near the negative end of the potential scan, followed by the typical re-oxidation or stripping peak (A1) upon reversing the potential scan. This feature could be attributed to the cathodic formation and the anodic dissolution of calcium. In the rest of the potential range,