Separation and Purification Technology 145 (2015) 24–28

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Ultrahigh purification in concentrated NaOH by electrowinning for solar cell application

Jiyong Joo [a,1], Jongwon Kim [b,1], Jin Won Kim [b], Joey D. Ocon [b], Jae Kwang Lee [a,b,*], Wook Chang [c], Jaeyoung Lee [a,b,*]

[a] Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, Gwangju Institute of Science and Technology, Gwangju 500-712, South Korea
[b] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea
[c] R&D Center, OCI Company, Ltd., Seongnam 462-120, South Korea

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 8 February 2015
Accepted 12 February 2015
Available online 23 February 2015

Keywords:
Electrowinning
High purity NaOH
Impurity-free Si wafers
Solar cell

ABSTRACT

High purity sodium hydroxide (NaOH) solution is extremely important in the large-scale manufacturing of impurity-free silicon (Si) wafers for solar cells. In this paper, we demonstrate the purification of highly concentrated NaOH *via* electrowinning. By optimizing temperature, current density, and the type of electrode for both anodes and cathodes, we maximized the selectivity toward cathodic deposition of Fe and Ni. Our results suggest that removal of metal impurities in the concentrated 50 wt.% NaOH is highly dependent on the reactor temperature (>90 °C) due to enhanced reaction kinetics and decreased solution viscosity. Meanwhile, current density has limited effect on the metal removal efficiency. We further demonstrate that the cathodic deposition of Fe and Ni strongly relies on the type of electrode pair used, with platinum (Pt) and nickel (Ni) as the anode and cathode, respectively, exhibiting the best removal performance. The good electrochemical performance arises from the high catalytic activity of Pt anode and good stability of Ni cathode from the highly corrosive concentrated alkaline conditions. Following these results, we recommend future scientific and technical studies on the use of electrowinning as a possible alternative to the costly membrane-based purification techniques.

1. Introduction

Globally, energy production with less or preferably without carbon dioxide (CO_2) emissions becomes one of the most emerging priorities that needed immediate actions because of the accelerated effects of global warming and the severe fossil fuel depletion within the recent decades. For this reason, solar energy – among a wide array of renewable energy sources – is considered as the most practical solution to this problem, being an almost unlimited resource and having minimal CO_2 production in its entire life cycle. Of late, significant efforts have been devoted to enhancing the conversion efficiencies of photovoltaic cells [1,2]. While dye-sensitized solar cells (DSSC) have garnered attention due to its low energy production cost per kilowatt-hour as well as its flexibility, the so – called 1st generation silicon (Si) photovoltaic devices continue to occupy almost 90% of the solar cell industry market due to its technological maturity and higher energy efficiency [1,3].

Production of high purity (99.99999% or 99.999999%, 7–8 N) polycrystalline Si wafers is a crucial step in making high efficiency solar cells [1,4,5]. In order to achieve such purity, 50 wt.% NaOH solutions are essentially used in polishing, cleaning and high temperature texturing of Si wafers during the fabrication process of Si wafer solar cell modules [1]. Unfortunately, impurities in the concentrated NaOH solutions, such as Fe, Ni, Pb and Cu, exist in commercial NaOH and the amount of impurities is compounded by the evaporator process (*e.g.*, 50 μM of Fe and 24 μM of Ni) and fluid transportation [3,4,6–8]. Hence, the presence of impurities represents a roadblock in improving the efficiency of Si solar cells, warranting their thorough removal from the NaOH solutions. To this end, companies such as Tsurumi Soda [9] and Toagosei [10] Co., Ltd., utilize ion exchange membranes (IEM) or resins in their purification systems. In the case of IEM, metal removal is achieved by separately capturing impurities into an anolyte chamber and then removing the precipitated impurities. While the purification process using IEM provides high metal recovery, still there are technical challenges in perfectly eliminating the impurities.

---

* Corresponding authors at: Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies (RISE), GIST, Gwangju 500-712, South Korea. Fax: +82 62 715 2434 (J. Lee).
E-mail addresses: na2522@gist.ac.kr (J.K. Lee), jaeyoung@gist.ac.kr (J. Lee).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.seppur.2015.02.011
1383-5866/© 2015 Elsevier B.V. All rights reserved.

Furthermore, replacing spent membranes result to additional removal costs [9,10].

In contrast to membrane-based systems, electrowinning as a one-step separation and purification process offers major advantages. First, the electrowinning system configuration is simple, which is composed of just two electrodes (anode and cathode) electrically connected to a power source. Second, impurities in the solution are directly reduced at the cathode [6–8]. Using this system, Lemos et al. [11] recovered Cu from wastewater effluents of gold processing plant. In another study, electrowinning was applied to recover zinc from an alkaline solution [12]. Furthermore, Allanore et al. [13] and Yuan et al. [8] investigated the electrochemical refinement method in making steel, which are produced during the carbothermic reduction of Fe_2O_3, with significantly reduced CO_2 emissions.

In this paper, we have investigated the optimal conditions for the metal impurity removal from a highly concentrated NaOH solution using electrowinning. The effect of temperature, applied current density, and the electrode configuration to the removal efficiency is demonstrated.

2. Experimental

Fig. 1 describes the schematic of the electrowinning cell. A rectangular Teflon cell was submerged in a water bath in order to control the temperature during experiments. The electrowinning cell contained 300 g of 50 wt.% of NaOH solution (OCI Company Ltd., Korea), with Fe and Ni concentrations of 50 μM and 24 μM, respectively. An overhead mechanical stirrer was used to maintain uniform temperature and enhance mixing within the cell. Every 20 min, 400 μg of the NaOH solution was collected from the cell. To measure the metal concentrations using inductively coupled plasma–mass spectrometry (ICP–MS), the NaOH solution was then diluted using 9.6 g of 6% HNO_3 solution. In addition, solution viscosity and conductivity of the NaOH solutions were measured using a viscometer (Visco Elite) and a conductivity meter (ECTestr 11 plus), respectively.

During electrochemical measurements, a potentiostat/galvanostat (Autolab PGSTAT1287N) was used as the current source. A pair of metal electrodes was immersed into the cell, with each electrode having a geometric surface area of about 18 cm^2. Ni foam and Pt mesh were used as electrowinning electrodes.

3. Results and discussion

The mechanism for the cathodic deposition of the metal impurities generally follows Eq. (1). The dependence of cell potential (E) on temperature and concentration can be described by the general form of the Nernst equation in Eq. (2),

$$M^{n+} + ne^- \rightarrow M(s) \quad (1)$$

$$E = E^o - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \quad (2)$$

where E^o is the standard equilibrium potential when the reaction quotient (Q) is unity, n is the number of electron/electrons that is/are involved in the reaction, $[M^{n+}]$ and $[M]$ are the concentrations of oxidized and reduced species in the solution, respectively, F is the Faraday constant, R, is the universal gas constant, and T is the absolute temperature. In the case of cathodic deposition, the reduced species concentration $[M]$ is just unity, allowing the simplification of Eqs. (2) and (3), by first defining the overpotential (η) as the difference between the cell potential and the standard equilibrium potential, $\eta = E - E^o$. The overpotential represents the additional energy expended for irreversible losses in the system (*i.e.*, heat) during electrowinning.

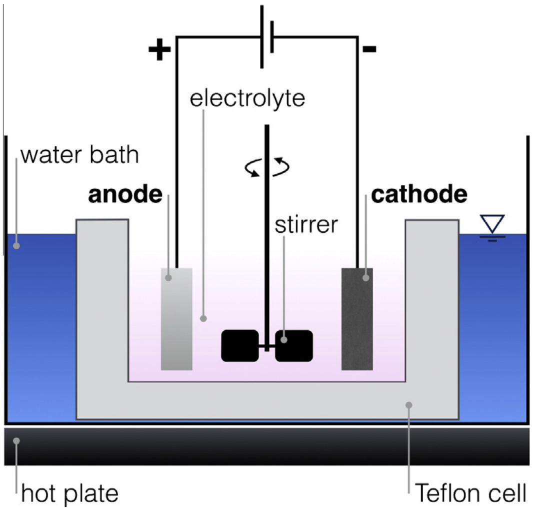

Fig. 1. Schematic diagram of electrowinning cell.

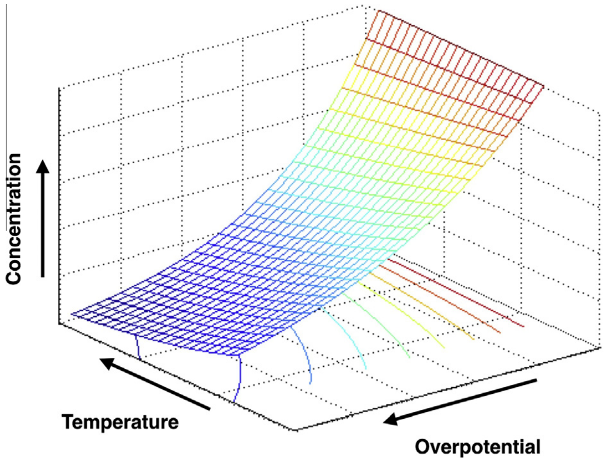

Fig. 2. Theoretical dependence of M^{n+} species to the overpotential and temperature during electrowinning.

$$[M^{n+}] = \exp^{\frac{nF\eta}{RT}} \quad (3)$$

To illustrate the theoretical dependence of M^{n+} species to the overpotential and temperature, we have plotted the equation in Fig. 2. As shown in the figure, concentration of M^{n+} species in the electrolyte sharply decreases with increasing overpotential and temperature. In the context of electrowinning, the higher the voltage/current density applied and temperature, the more efficient is the cation removal process.

In order to see the relationship between voltage and temperature, cell voltage was measured at different temperature at a fixed current density of 0.5 A/cm^2, as shown in Fig. 3. Apparently, cell voltage gradually decreased with increasing temperature due to enhanced conductivity leading to decreased solution resistance. On the basis of Fig. 2, illustrating the theoretical dependence of overpotential and temperature, overpotential is highly depended on the temperature. Notably, voltage does not be stable at 75 °C and 95 °C until 20 min, while it is stable at 105 °C. It is believed that the ionic mass transfer is limited until equilibria of redox reaction at 75 °C and 95 °C due to high viscosity even though the reactor is homogeneously agitated. On the other hand, the system shows steady voltage variation when it is close to the boiling point