Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Electroanalytical Chemistry 575 (2005) 195–202
Journal of Electroanalytical Chemistry
www.elsevier.com/locate/jelechem

Electrocrystallization of calcium carbonate on carbon-based electrodes

J. Rinat [a], E. Korin [b], L. Soifer [b], A. Bettelheim [a,b,*]

[a] *Nuclear Research Centre, P.O. Box 9001, Beer-Sheva 84190, Israel*
[b] *Department of Chemical Engineering, Ben Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel*

Received 16 June 2004; received in revised form 14 September 2004; accepted 15 September 2004
Available online 11 November 2004

Abstract

Calcium carbonate was deposited by electrochemical reduction of oxygen to hydroxyl ions at various carbon-based electrodes. Although some vaterite was observed during earlier stages of the electrodeposition, the predominant polymorph during later stages was calcite. The average crystal size reached a value of 15 μm after 10 h at a glassy carbon electrode but the crystal growth rate was substantially accelerated when oxygen was catalytically reduced. The same average size of the calcite crystals in this case (Pt/C electrode) was reached within a period of 1.5 h. Efficient removal of $CaCO_3$ from water was demonstrated when using a porous aerogel carbon electrode and a potential sufficiently negative to promote reduction of water molecules within the pores.

Keywords: Calcium carbonate; Precipitation; Scaling; Crystallization; Electrochemical; Carbon electrodes

1. Introduction

Calcium carbonate scaling is often a major problem in the natural water supply of industrial plants and various chemical engineering processes. The precipitation and crystallization of calcium carbonate as an insulating layer causes a decrease in the flow rate in pipes and causes reduced heat transfer in heat exchangers. Precipitation of $CaCO_3$ in ground water also influences the storage, transfer and oxidation of aquifers. There are numerous reports dealing with water treatment [1,2], chemical and physical scale prevention and estimation of the treatment efficiency [3–6].

Addition of chemical reagents to the water, even in trace amounts, is sometimes undesired, such as in biological systems. The present study deals with removal of calcium ions from water by controlled electrochemical deposition and crystallization of $CaCO_3$. This method, which does not involve addition of scaling inhibitors [6–8], is based upon reduction of dissolved oxygen in water according to the reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-. \quad (1)$$

At more negative potentials, water reduction occurs with a formation of hydrogen gas

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

The formation of hydroxide ions is followed by precipitation of $CaCO_3$ on the electrode surface:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (3)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (4)$$

Electroprecipitation of $CaCO_3$ on several electrodes, such as carbon steel [9], nickel [10], copper [11], bronze and noble metals including vitreous carbon [12], stainless steel [13,14] and gold [6] has been studied and has also included visualization of the crystallization

---

[*] Corresponding author. Tel.: +97 28 6461799; fax: +97 28 6477656.
E-mail address: armandb@bgumail.bgu.ac.il (A. Bettelheim).

0022-0728/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2004.09.011

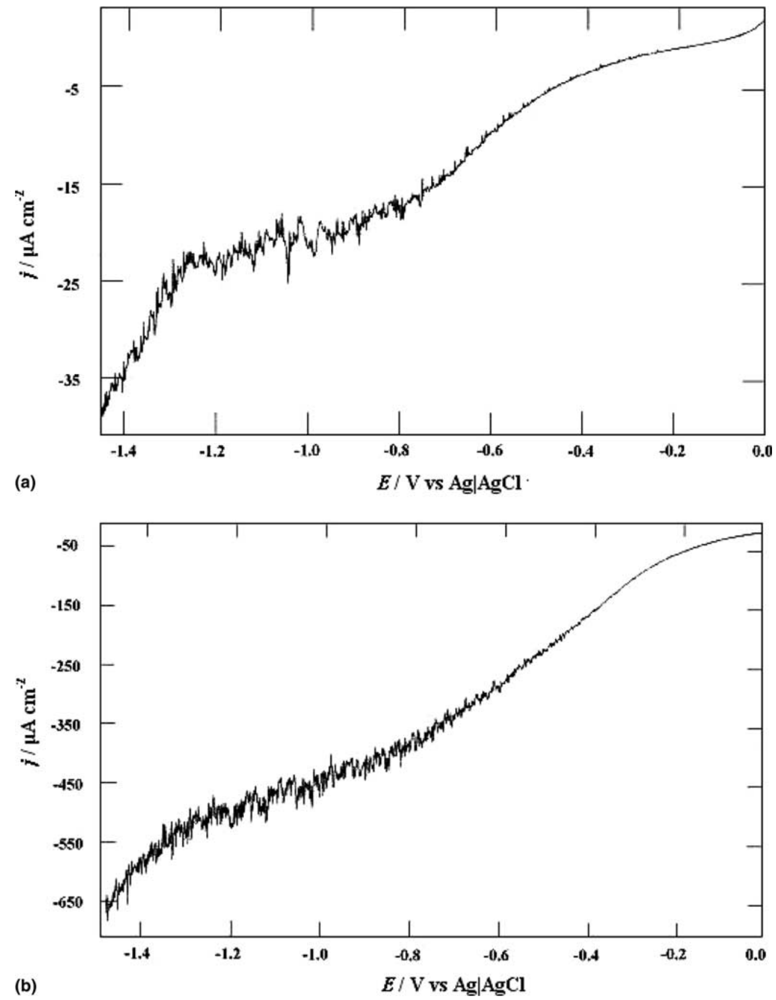

Fig. 1. Linear sweep voltammogram at a scan rate of 20 mV/s for oxygen reduction at GC (a) and graphite (b) electrodes in a solution containing 4.5 mM $NaHCO_3$ + 3 mM $CaCl_2 \cdot 2H_2O$ and continuously supplied with air (flow rate: 100 ml/min).

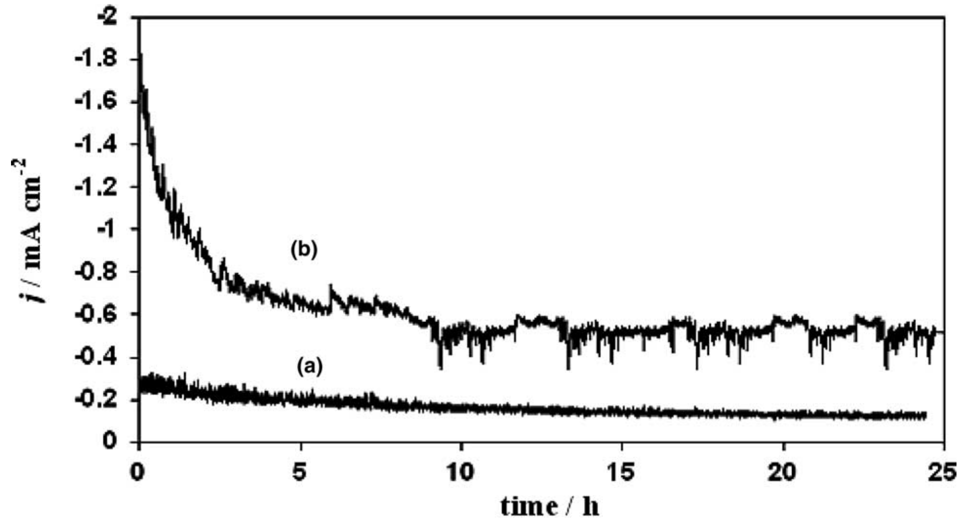

Fig. 2. Chronoamperometric curves obtained at −0.9 V for GC (a) and graphite (b) in a solution bubbled with air and with the same composition as mentioned in Fig. 1.