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Electrochemical study of calcium carbonate deposition on iron. Effect of the anion

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ABSTRACT

Deposition of calcium carbonate on iron from supersaturated solutions containing 1 M sodium chloride, bromide, iodide, or nitrate as supporting electrolyte was studied at 60 °C under open-circuit conditions using impedance spectroscopy, chronopotentiometry, voltammetry, and scanning electron microscopy. The anions were found to fall into two groups with respect to their effect on scaling. On the one hand, chloride and, especially, nitrate favor faster scaling kinetics and lead to compact carbonate films composed of entangled aragonite crystals. On the other hand, in the presence of bromide and iodide the scaling rate is lower and the resulting films feature aragonite crystals more or less freely scattered on what appears to be a uniform sublayer of unknown structure. The experimental data are adequately described using quasi-uniform film model accounting for the cathodic and anodic electrode reactions. As deduced from the electrochemical measurements, the barrier properties of the carbonate films formed in different supporting electrolytes increase in the order of $Cl^- < NO_3^- \approx Br^- < I^-$.

1. Introduction

Practical importance of carbonate scaling to many industrial applications has prompted numerous investigations into the process of calcareous scale formation on metal surfaces. But it was not until the second half of the 1990s that this area of research started to become actively explored by the electrochemists. This surge of interest coincided with the advent of ‘electrocrystallization’ or ‘accelerated electrochemical scaling’, a convenient means of generating carbonate deposits on conducting surfaces. The procedure consists of cathodic polarization of the working electrode at potentials ranging from −0.8 to −1.75 V/SCE in aqueous solutions containing Ca^{2+} and HCO_3^-/CO_3^{2-} ions. It results in local pH increase in the diffusion layer, due to the dissolved oxygen and/or water reduction at the electrode, shifting chemical equilibrium towards carbonate precipitation. Substrates studied include noble metals [1–4], Fe [5], Ni [6], Cu [7], various kinds of steel [8–15], and, lately, ITO [16] and carbon-based materials [17].

Electrocrystallization is attractive from the experimental point of view since by varying the potential program it allows to control growth rate, amount, and morphology of the deposit. It was observed by SEM that maintaining the potential at −1.1 V/SCE leads to aragonite, while at −1.75 V/SCE only calcite is formed, each polymorphic modification exhibiting its characteristic impedance response [13,14]. Common to all impedance experiments is the increase in its magnitude with time due to progressive surface blocking by the salt film, as testified by the appearance of high-frequency loop supplementary to flattened capacitive loop at high deposition times [3,13]. This impedance behavior was ascribed to diffusion-controlled oxygen reduction in pores [1–3,5].

In the majority of studies scaling solutions modeled fresh or sea water, with Ca^{2+} concentration in the submillimolar to millimolar range. Since in the natural waters calcium is always present along with magnesium, additions of the latter cation were featured in several works [4,6,12] and found to favor precipitation of aragonite rather than calcite at room temperature. Apart from carbonate and bicarbonate, chloride anions were typically introduced into scaling solution in concentrations up to 0.5 M. Although no extensive investigations of the anion influence on scaling have been attempted, contrasting descriptions of the effect of sulfate [4,15] and a brief mention of nitrate [4] increasing the rate of calcium carbonate precipitation can be found in the literature.

Recent emphasis in the research on calcareous scaling is placed on developing and validating nucleation-growth models under cathodic polarization using combination of in situ experimental techniques. Along these lines Devos et al. [18,19] have presented several elegant studies in which carbonate deposition at cathodic potentials was simultaneously monitored by optical microscopy, EQCM, and either electrochemical impedance or chronoamperom-

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etry. Optical microscopy has also been employed to investigate the effect of the metallic substrate [7].

While electrocrystallization studies have furnished valuable data on calcareous deposits, in practice carbonate scaling of metal surfaces usually takes place under zero net current conditions. In this case salt film formation occurs together with metal dissolution and buildup of corrosion products. Such studies are few [5,20,21] compared to those at cathodic polarization. Still fewer experiments are reported [21] that deal with high supersaturations, ionic strength, and elevated temperatures, characteristic, for example, of oil wells. This paper supplements the paucity of experimental data obtained at the corrosion potential and represents the first systematic study of carbonate scale formation in the presence of monovalent anions.

2. Experimental

All electrochemical measurements were performed at 60 °C in a three-electrode cell containing 80 mL of electrolyte prepared immediately prior to each experiment by mixing equal volumes of preheated solutions containing calcium and bicarbonate ions so that the resulting mixture contained 0.05 M CaX_2 (X = Cl, NO_3), 1 M NaY (Y = Cl, Br, I, NO_3), and 0.025 M $NaHCO_3$. The working electrode was Armco iron disk (2 cm^2) cleaned with emery paper (1000 grade) and rinsed with ethanol and distilled water before use. Pt counter electrode was oriented parallel to the working electrode. The potential was measured with respect to Ag/AgCl reference electrode. Solartron 1287 electrochemical interface/1255 frequency response analyzer controlled by ZPlot2© and CorrWare2© software were used to acquire impedance data at the corrosion potential and voltammograms. SEM images were obtained on Hitachi S-3400N electron microscope.

3. Results and discussion

Shown in Fig. 1 are the capacitance and resistance measured at 10 kHz in 0.05 M $CaCl_2$ + 1 M NaY (Y = Cl, Br, I) + 0.025 M $NaHCO_3$ following immersion into the scaling solution. In agreement with the previous studies, the capacitance at high frequency gradually decreases, while the resistance steadily increases with time due to the film of calcium carbonate forming on the surface. For all three anions the initial capacitance values lie around 20–25 $\mu F\,cm^{-2}$, the end values being 2–4 $\mu F\,cm^{-2}$. The resistance grows by a factor of 3–4 over the course of experiment. Both sets of curves point to the differences in the scaling process in the presence of chloride and the heavier halides. Although the end values are similar, the capacitance decay in the former case is notably faster. In the chloride medium the resistance curve is S-shaped, while no regions of decreasing slope are observed in added NaBr or NaI.

As compared to bromide and iodide, nitrate ion appears to have an opposite effect on the rate and magnitude of change of the impedance components at 10 kHz if one takes the chloride solution as a reference (Fig. 2). In 0.05 M $Ca(NO_3)_2$ + 1 M $NaNO_3$ + 0.025 M $NaHCO_3$ the capacitance falls off considerably more rapidly, reaching 1 $\mu F\,cm^{-2}$, and the resistance increases to a value more than three times higher than in the presence of chloride. However, despite these variations in the capacitance and resistance the curves for chloride and nitrate bear clear shape resemblance.

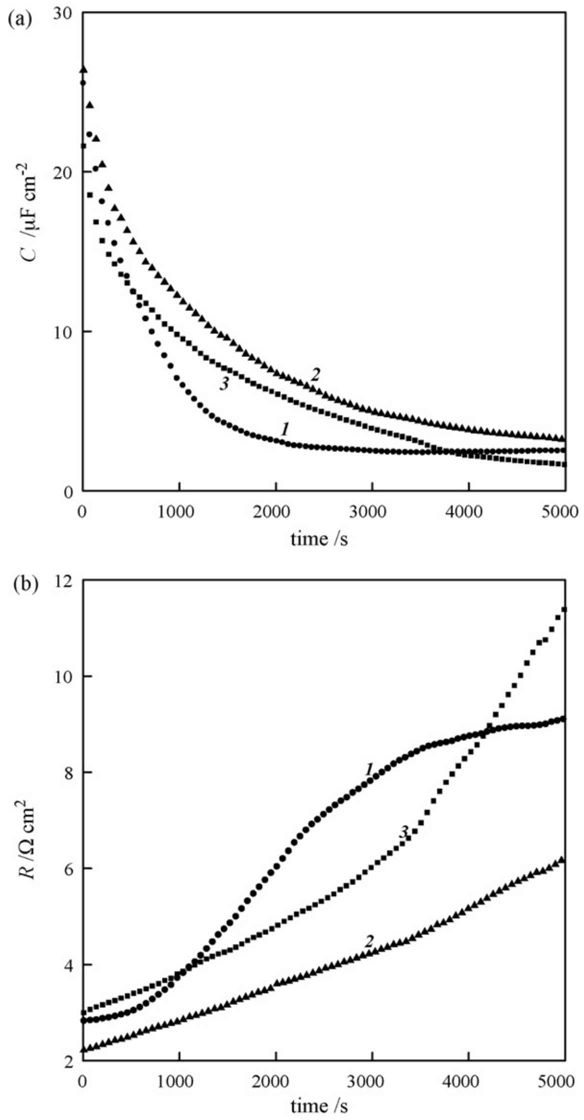

Fig. 1. Capacitance (a) and resistance (b) at 10 kHz in 0.05 M $CaCl_2$ + 1 M NaY + 0.025 M $NaHCO_3$: (1) Y = Cl; (2) Y = Br; (3) Y = I.

In order to verify that the observed differences in the behavior of the impedance components at high frequency in the scaling solutions containing various anions are connected mainly to the process of salt film deposition and not the simultaneously occurring corrosion, analogous experiments were performed in solutions without bicarbonate. The corresponding capacitance curves are plotted in Fig. 3. It is seen that, except for nitrate, showing some capacitance growth in the beginning, there is little variation in the capacitance values over the period of time it took the capacitance to decrease almost by an order of magnitude in the solutions with bicarbonate. Halide capacitance curves are progressively shifted downward going from chloride to bromide, which is expected bearing in mind stronger specific adsorption (chemisorption) in the series. For nitrate the capacitance falls back to its initial values and after 2000 s follows the same trend as the other anions. The capacitance peak at 1000 s in the nitrate solution can be explained by the electrode reactions involving this anion as discussed in more detail below. Contrary to the scaling solutions, in the absence of bicarbonate the resistance at high frequency is nearly constant for all anions (not shown).

The imaginary part of impedance at 10 kHz is dominated by the double layer capacitance. Its behavior can be rationalized in terms of the simple Helmholtz model stating that the capacitance of the electric double layer is directly proportional to its dielectric constant and inversely proportional to its thickness. Both of these factors contribute to the capacitance decay since calcium carbonate is an insulator with a rather low dielectric constant (8.3 for calcite