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Short communication

The role of temperature on the corrosion and passivation of type 310S stainless steel in eutectic (Li + K) carbonate melt

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Abstract

The corrosion behavior of type 310S stainless steel was studied in the eutectic Li + K carbonate as a function of temperature by several electrochemical methods. Within the range 600–675 °C the steel passivated spontaneously at OCP condition after a few hours of immersion. Active-passive transition was observed in the polarization curves below 600 °C and above 675 °C indicating a failure to reach a stable passive condition even at prolonged exposure times. Impedance analysis indicates that passivity does not lead to the formation of an impervious barrier layer as denoted by the presence of diffusional components at low frequencies indicating oxide growth. Corrosion rates exhibited a minimum at 675 °C at both OCP and at cathode polarization conditions. A mechanism to explain the active–passive transition has been proposed based on the phase transition from $LiFe_5O_8$ to $LiFeO_2$.

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1. Introduction

Austenitic 316L and 310S stainless steels are the most commonly used materials for the construction of bipolar plate components in the molten carbonate fuel cell (MCFC) technology because of good compromise between corrosion resistance and oxide scale resistivity at 650 °C under standard operating conditions. In detail, type 310S steel exhibits a much slower oxide growth rate, although 316L steel is sometimes preferred as its oxide scale has a higher electrical conductivity [1]. The corrosion resistance of these steels basically relies on the rapid formation of a protective passive oxide scale that is able to suppress the outward diffusion of base-metal cations (mainly, iron) into the molten electrolyte. After long test periods, the two-layered structure of the passive scale consists of an external $LiFeO_2$ layer and an inner Cr-rich oxide layer. The passivity of stainless steels depends on the stability of this inner layer [1,2]. In the case of the high-Cr type 310S steel (ca. 25 wt.%), the Cr-rich oxide layer is composed mainly of a compact, thin and corrosion resistant layer of $LiCrO_2$ which strongly hinders the iron diffusion, thus limiting the growth of the external $LiFeO_2$ layer. Conversely, the 316L steel forms higher inner conductive spinel layer mainly consisting of $LiFe_5O_8$ and $FeCrO_4$ phases. The spinel layer is less effective in retarding the outer iron diffusion, thus leading to a faster growth of the external $LiFeO_2$ layer and to an overall higher thickness of the scale [1,3].

Since MCFC stack operations result in large temperature variations (580–700 °C) along the surface of bipolar plates it would be important to evaluate the steel corrosion as a function of temperature, although this aspect has been scarcely investigated in literature. For instance, the authors of Refs. [2,4] report that the corrosion of 316L steel becomes highly sensitive on the reaction conditions in the eutectic Li + Na carbonate melt during cell start-up. At temperatures as low as 600 °C this steel seems to become highly susceptible to corrosion damage with a pitting-like attack in high CO_2 gases. Obviously, the possibility of a localized corrosion is a real concern for the use of the 316L steel in alternative alkali carbonate compositions based on the Li + Na electrolyte.

As part of a work aimed to analyze the corrosion behavior of 316L and 310S steels in Li + K and Li + Na carbonates, we will present some results on the stability of the passive scale forming on the 310S stainless steel surface in Li + K melt in the temperature range 580–700 °C. This study has been mainly conducted by electrochemical methods with emphasis to the measurements of

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open circuit potential, anodic polarization curves and impedance spectra.

2. Experimental

Working electrodes for the electrochemical measurements were machined from a 1-mm thick sheet of commercial type 310S austenitic stainless steel. The electrodes were shaped to 10 mm × 10 mm squares. The surface of the samples was mechanically polished with water-cooled SiC paper up to 600 grit with the residues removed by a short ultrasound treatment in high-purity water. The electrode holder was made by spot welding the sample back face to a gold lead wire, which was inserted in a thin alumina tube. The back face was then sealed with alumina cement. A gold foil (10 mm × 10 mm) was used as counter-electrode, whereas a gold wire dipped in the eutectic $(0.62Li + 0.38K)_2CO_3$ mixture under CO_2–O_2 gas (0.667–0.333 atm) and contained in a alumina tube served as oxygen reference electrode. The liquid contact with the working electrode compartment was assured by a small pinhole in the reference tube.

The apparatus for electrochemical experiments consisted in an alumina pot-cell as described elsewhere [5]. The electrolyte used for this work consisted in a solution of Li_2CO_3 and K_2CO_3 salts mixed at the eutectic composition (62 mol% Li_2CO_3 and 38 mol% K_2CO_3). Fifty grams of salt were used to ensure that the electrodes were totally immersed in the electrolyte during experiments. All gas mixtures were at a total pressure of 1 atm. The total gas flowrate was set a $100\,cm^3\,min^{-1}$ by an Aalborg thermal mass flowmeter.

The electrochemical measurements were made by using computer-controlling equipments consisting of a potentiostat/galvanostat (EG&G 173) and a lock-in amplifier (EG&G 5301). Polarization scans were carried out at a rate of $1\,mV\,s^{-1}$. EIS measurements were carried out at OCP conditions with the fast Fourier transform (FFT) technique instead of the more time-consuming single-sine technique.

After the corrosion tests analysis of the corrosion products was conducted by XRD on selected electrodes.

3. Results and discussion

3.1. Open circuit potential (OCP) measurements

The OCP variation of type 310S stainless steel at various temperatures of relevance to MCFC was followed as a function of immersion time until a steady state condition is established (Fig. 1). It is known that such kinds of measurements can provide useful information on the formation of stable passive scale taking into account that metallic corrosion in molten salts can be usually described as the sum of two basic processes, namely anodic metal oxidation (eventually leading to passivation) and oxide scale dissolution.

Thus, from Fig. 1 we can observe that OCP reaches a stable condition with increasing anodic values at increased temperature in the range 575–675 °C, whereas at 695 °C the OCP falls in the cathodic direction at a value lower than that at 575 °C. These facts indicate a temperature raising from 575 to 675 °C favours the onset of passivity and a general corrosion resistance improvement. On the other hand, the OCP behavior at 695 °C is a clear indication of some dissolution of the oxide scale thus leading to a degradating protectiveness of the steel surface.

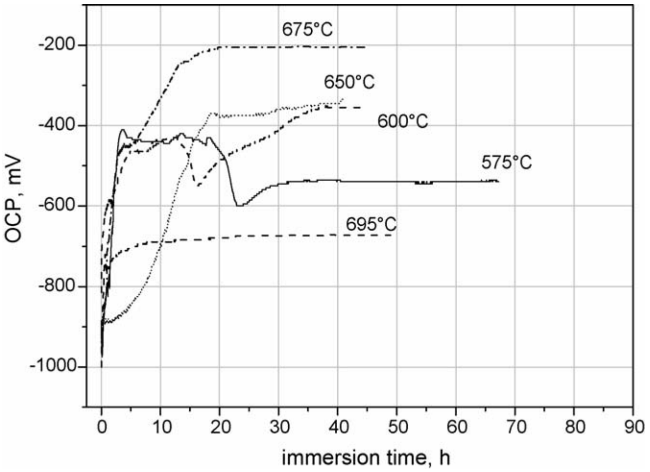

Fig. 1. OCP of type 310S stainless steel as a function of temperature in the Li + K carbonate under standard cathode gas.

3.2. Polarization curves

The use of short-term polarization tests for life-time prediction is mainly based on the assumption that the same corrosion process should hold good over a long time span. This may be not true for alloys such as type 310S steel that rapidly develop increasing corrosion resistance over the time. Therefore, polarization curves were acquired at the end of OCP experiments when a stationary surface condition was clearly reached.

Polarization scans were observed to deeply alter the surface of the passive steel electrode in molten carbonates for currents exceeding several $mA\,cm^{-2}$ [6]. Care was therefore taken to acquire curves avoiding large cathodic overpotentials and ending anodic scans at 0 mV. However, for actively corroding electrodes such as the sample at 695 °C, surface perturbations induced by deep polarization were less evident.

Fig. 2 illustrates the potentiodynamic polarization response of type 310S at various temperatures. Active–passive transition was clearly observed at both 575 and 695 °C indicating that at these temperatures the steel was not able to reach a passive condition under OCP. Conversely, the polarization curves in the range 600–675 °C showed a fully passive behavior with similar passive current densities. The active–passive peak are observed at about −350 mV.

3.3. Potential decay measurements

The absence of passivity at 695 °C was also confirmed by potential decay measurements. On stable electrodes an anodic current of $10\,mA\,cm^{-2}$ was applied for 1 min to create strong melt acidity conditions, i.e. production of CO_2. Due to the slow recombination reaction ($CO_2 + O^{2-} = CO_3{}^{2-}$), this treatment

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