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Performance studies of bare and Co-plated titanium alloy as cathode current collector in Molten Carbonate Fuel Cell (MCFC)

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Abstract

The corrosion characteristics of bare, heat treated and cobalt coated titanium alloys were studied and compared with that of SS 316 in molten carbonates (Li/K = 62/38 vol.%) at 650 °C under oxygen atmosphere using electrochemical and surface characterization techniques. Immersion test of titanium alloys conducted in cathode environment followed by atomic absorption spectroscopy (AAS) indicated leaching of molybdenum from the alloy. Coating the alloy with Co was found to decrease the molybdenum dissolution rate. X-ray diffraction results showed the formation of $LiTiO_2$ and Li_2TiO_3 on the surface of the titanium alloys and formation of $LiFeO_2$ and Fe_2O_3 in the case of SS 316. SEM and EDAX analysis of the post-test samples revealed the loss of Mo, Sn and Zr from the titanium alloys and loss of Cr and Ni from SS 316. Electrochemical studies showed that the conductivity of the corrosion scale was higher for cobalt electroplated alloy when compared to other titanium alloys and lower than that of SS 316. Cobalt coated titanium alloy exhibited higher polarization resistance than other alloys. The present study confirmed that the surface modification of titanium alloy lead to the formation of a protective layer with better corrosion barrier properties and better electronic conductivity in molten carbonate fuel cell cathode operating conditions.

Keywords: Molten carbonate fuel cells; Cathode current collector; Dissolution; Titanium alloys; SS 316

1. Introduction

The Molten Carbonate Fuel Cell (MCFC) operating at 650 °C has been under intensive development for the last few decades as a second-generation fuel cell [1,2]. System efficiency and cost of the MCFC appear very attractive when compared to other low temperature fuel cells. State-of-the-art MCFC cell design comprises of a Ni–Cr anode, NiO cathode and γ-$LiAlO_2$ matrix impregnated with 62:38 mol% Li_2CO_3 and K_2CO_3 as an electrolyte retention matrix. Austenitic stainless steels such as 310S, 316 or 316L are typically used for cathode current collectors and bipolar separator plates [3–7]. Corrosion of these steel components is a major lifetime-limiting factor in molten carbonate fuel cells. The steel components are subjected to a large polarization when they are used in the cathode side owing to the potential at which oxygen reduction reaction occurs. This polarization leads to the oxidation of stainless steel components and to dissolution of some of the alloy components through the porous corrosion scales. The corrosion resistance of stainless steels and nickel-base alloys in aqueous solutions can often be increased by addition of chromium or aluminum [8–10]. Chromium protects the base metal from corrosion by forming an oxide layer at the surface. Chromium containing stainless steel however, leads to the induced loss of electrolyte. Previous studies done to characterize the corrosion behavior of chromium in MCFC conditions have shown formation of several lithium chromium oxides by reaction with the electrolyte [8]. This corrosion also results in an increase of the Ohmic loss due to formation of scales on the steel. Aluminum addition has a positive effect on corrosion resistance [9,10]. However, corrosion scales formed in aluminum containing alloys show low conductivity leading to a significant Ohmic polarization loss.

Pure titanium has been used as a cathode current collector for MCFC because of its low solubility in the alkaline carbonate

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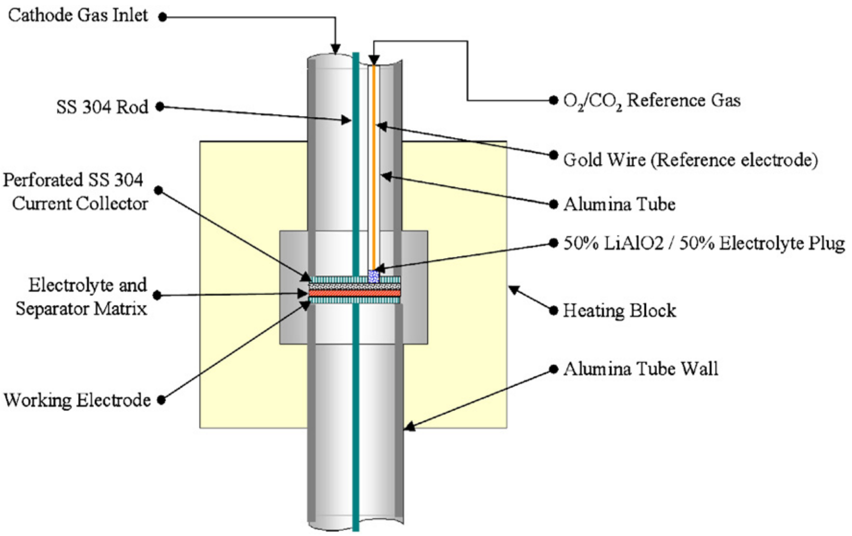

Fig. 1. Schematic diagram of the 7-cm^2-electrochemical half-cell.

melt under cathode atmosphere [11–15]. Thermodynamically, lithium titanate (Li_2TiO_3) is the stable species in both cathodic and anodic atmosphere. The protective oxide layer on Ti surface has a low conductivity value, which increases the Ohmic losses in the cell. It has also been shown that alloying titanium with nickel brings the conductivity value of the alloy higher than titanium, but lower than nickel [11]. Ti oxides that are protective in nature lead to higher Ohmic losses. The performance of these materials can be improved through surface modification. In a separate study we observed that a layer combining the low solubility of cobalt oxide and high conductivity of nickel oxide is able to increase the conductivity of the oxide scale on SS304 and at the same time protect the alloy [16]. A survey of materials used at high temperatures revealed that apart from austenitic steels, titanium alloys have excellent corrosion and mechanical resistance.

In this work, our goal was to characterize the performance of a titanium alloy with different surface treatments, which could be used as a cathode current collector.

2. Experimental

Three electrodes of area 7 cm^2 were cut from 0.42 mm Titanium Alloy Beta 3 (Ti77.5/Mo12/Zr 4.5/Sn 4.5) sheets purchased from Goodfellow. The electrodes were polished with alumina powder, cleaned with alkali and rinsed with distilled water in order to be free of any contaminants or oxides. One of the electrodes was used as received and the second electrode was heat treated at 400 °C in 99% nitrogen and 1% oxygen atmosphere for 62 h to promote the growth of a more uniform and thicker oxide layer [17] and used for testing. The third electrode was used for cobalt electro-deposition. A layer of cobalt was electrodeposited on the surface of a titanium alloy to improve the conductivity of the oxide layer. Cobalt coating on titanium alloy specimens was carried out at room temperature in a solution containing 12 g/l cobalt chloride, 105 g/l sodium citrate, ammonium hydroxide and 0.3 g/l dextrin. Prior to electroplating, the specimens were etched in a solution of HF and HNO_3. Electro-deposition was done at pH 9.5 for 2.5 h at a current density of 1 mA/cm^2 and the specimens were rinsed with distilled water. The film thickness was calculated to be 1 μm.

In order to determine the solubility of the corrosion products of the alloys, immersion tests were carried out under cathode gas conditions. Square electrodes of area 1 cm^2 were cut from fresh Ti alloy, heat-treated Ti alloy, Co coated Ti alloy and SS 316. The samples were immersed in alumina crucibles containing 100 g of molten carbonate (Li/K = 62/38 mol%) at 650 °C. Cathode gas (30% CO_2/70% air) was bubbled through the carbonate melt using alumina tubes. About 0.4 g of molten carbonate was taken from the melt approximately every 24 h using an alumina rod. The electrolyte samples were dissolved in 40 ml of 10% dilute acetic acid. The samples were analyzed using a Perkin Elmer 3300 atomic absorption spectrometer (AAS) to determine the concentration of dissolved chromium, nickel and molybdenum in this solution. Immersion studies were carried out for 350 h.

Electrochemical studies were performed in a 7 cm^2 lab scale half-cell shown in Fig. 1. The cell consists of a stainless steel support, the working electrode, the electrolyte-separator matrix, a stainless steel counter electrode and a reference electrode consisting of gold wire (Au/67%CO_2/33%O_2) connected to the electrolyte tile with a salt bridge (50%$(Li_{0.62}K_{0.38})_2CO_3$ + 50%$LiAlO_2$). $(Li_{0.62}K_{0.38})_2CO_3$ eutectic embedded in a $LiAlO_2$ matrix was used as the electrolyte. Oxidant gas composition of 67% CO_2 and 33% O_2 was passed to the working electrode. Polarization studies were performed using an EG and G PAR model 273A potentiostat interfaced with a computer. Electrochemical impedance spectroscopic studies were performed using Model 1255 Schlumberger Frequency Analyzer. The impedance data generally covered a frequency range of 1 mHz to 100 kHz. A sinusoidal ac voltage signal varying by ±5 mV was applied in all cases.

After testing, the samples were immersed in diluted acetic acid and rinsed with distilled water to remove the eutectic