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Project Title:
Optimization of the Cathode Long-Term Stability in Molten Carbonate Fuel Cells: Experimental Study and Mathematical Modeling

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Abstract

SS 304 was encapsulated with thin layers of Co-Ni by an electroless deposition process. The corrosion behavior of SS304 and Co-Ni-SS304 was investigated in molten carbonate under cathode gas atmosphere with electrochemical and surface characterization tools. Surface modification of SS304 reduced the dissolution of chromium and nickel into the molten carbonate melt. Composition of the corrosion scale formed in case of Co-Ni-SS304 is different from SS304 and shows the presence of Co and Ni oxides while the latter shows the presence of lithium ferrite. Polarization resistance for oxygen reduction reaction and conductivity of corrosion values for the corrosion scales were obtained using impedance analysis and current-potential plots. The results indicated lower polarization resistance for oxygen reduction reaction in the case of Co-Ni-SS304 when compared to SS304. Also, the conductivity of the corrosion scales was considerably higher in case of Co-Ni-SS304 than the SS304. This study shows that modifying the current collector surface with Co-Ni coatings leads to the formation of oxide scales with improved barrier properties and electronic conductivity.
Introduction

The Molten Carbonate Fuel cell (MCFC), operating at a temperature of 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 operating fuel cells. State of the art MCFC cell design comprises of a Ni-Al anode where hydrogen is oxidized to water and NiO cathode where oxygen and carbon dioxide are reduced to carbonate ions. Austenitic stainless steels like 310S, 316 or 316L are typically used for the construction of cathode and anode 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 huge polarization when they are used in the cathode side owing to the potential in which oxygen reduction reaction occurs. This polarization leads to the oxidation of stainless steel components and to the dissolution of some of the alloy components through the porous corrosion scales. The corrosion behavior of stainless steel components in molten carbonate conditions has been studied extensively during the past decade. Research is being aimed at increasing the corrosion resistance of these components by altering the alloy composition [3,4,8-11] or by surface modification techniques [12,13].

The corrosion resistance of stainless steels and nickel-base alloys in aqueous solutions can often be increased by addition of chromium or aluminum [14-16]. Chromium protects the base metal from corrosion by forming an oxide layer at the surface. Previous studies done to characterize the corrosion behavior of chromium in MCFC conditions have shown the formation of several lithium chromium oxides by reaction with the electrolyte [14]. This corrosion process also results in increased ohmic loss due to formation of scales on the steel. Similarly, aluminum additions have a positive effect on corrosion resistance [15,16]. However, corrosion scales formed in aluminum containing alloys show low conductivity leading to a significant ohmic polarization loss.

Surface modification of the current collectors by suitable coatings, (electroless plating, electro cladding etc.) is an alternate approach to solving the corrosion problem. Surface modification or alloying alters the composition and complexity of the corrosion scales, which prevent the further corrosion and outward diffusion of alloy components. The coating materials that are currently researched fall into three categories namely (i) metals and alloys, (ii) ceramics composed of non-metals and (iii) ceramics composed of metals and non-metals including mixed
oxides. Most of the current research on corrosion protective coatings is aimed at metals and alloys especially because of the conductivity demand. Nickel electro cladding is popularly used as a surface modification technique to reduce corrosion on the anode side of the bipolar plate. However, the corrosion performance of most of the metals is not satisfactory on the cathode side. Ceramic coatings have good corrosion resistance properties, but they have poor electronic conductivity. Mixed oxides are more or less stable in molten carbonate (e.g. Li doped NiO, LiCoO$_2$, LiFeO$_2$ etc.). This is evident from the fact that they are themselves the corrosion products in molten carbonates. Therefore, oxide materials can be used as coating to impart barrier properties and corrosion resistance in molten carbonates.

Nickel containing scales exhibit higher conductivity due to the presence of trivalent nickel ions, which introduce vacancies in the lattice of the scale [17]. Therefore nickel based coating can lead to superior conductivity and good protection provided that it is alloyed properly with corrosion resistant elements. Cobalt has a lower solubility in molten carbonate [18]. Electroless plating of Ni-Co gives rise to deposition of uniform layers of nanostructured material, which would result in better protection of the substrate. The objective of this work is therefore to synthesize electroless Co-Ni over SS 304 substrate and characterize it in MCFC cathode conditions. We expect to form a layer of lithiated Co-Ni oxides, which would not only improve the corrosion resistance but also increase the electronic conductivity. The corrosion characteristics of both SS304 and Co-Ni-SS304 have been studied using a variety of electrochemical and surface characterization techniques. Flame atomic absorption spectroscopy has been used to analyze the dissolved metal concentrations in molten carbonate.

Experimental

Electrodes of area 1 cm$^2$ were made from a perforated stainless steel 304 (Perforated Metals Inc.), with a void area of 45%. The electrodes were cleaned with alkali and were washed in distilled water before the characterization studies in order to be free of any contaminants. Co-Ni encapsulation on SS304 electrodes was carried out using a procedure developed in our laboratories. The deposition was carried out in a bath of composition 14 g/L NiSO$_4$, 5 g/L CoSO$_4$, 20 g/L NaH$_2$PO$_2$, 60 g/L sodium citrate and 65 g/L ammonium sulphate. The pH was maintained between 8.5-9 by addition of ammonium hydroxide. The temperature was between 85-95°C. By varying the amount of cobalt sulphate in the bath different ternary alloys of Ni-Co-
P can be obtained [19]. The Co-Ni encapsulated SS304 was rinsed with deionized water and subsequently dried at 65°C for 4 hours.

In order to determine the solubility of the corrosion products and the coating material in molten carbonate, immersion tests were carried out under cathode gas conditions. Square electrodes of area 1 cm² were cut out from SS 304 and Ni-Co encapsulated SS 304. They were weighed and were carefully dropped inside an alumina crucible containing 100 g of molten carbonate (Li/K=62/38 vol.%) at 650°C. Cathode gas (30% CO₂/70% air) was bubbled through the carbonate melt using alumina tubes. About 0.5 g of molten carbonate was taken from the melt approximately every 6 hours using an alumina rod. The molten carbonate sample was dissolved in 10% dilute acetic acid. Atomic absorption spectroscopy was used to analyze the concentration of dissolved nickel and chromium concentrations. Immersion studies were carried out for 200 hours after the start of the experiment.

In-situ oxidation of bare and surface modified SS 304 electrodes were studied using a three-electrode set-up. Square electrodes (1 cm x 1 cm) cut from bare and surface modified SS304 were spot welded with a gold wire and was used as the working electrode. Gold was used as the counter electrode and Au/(2CO₂+1O₂) served as the reference electrode. The reference gas flow rate was maintained at 10 cc/min. Oxidant gas with a composition of 30% CO₂ and 70% air (National Welders) was directly purged into the (Li₀.₆₂K₀.₃₈)₂CO₃ eutectic melt through an alumina tube. The open circuit potential studies were done using an EG&G PAR model 273A potentiostat interfaced with a computer. The oxidation behavior was also studied by using cyclic voltammetry method.

Tafel polarization studies, impedance analysis and i-V polarization studies were carried out using a 3 cm² lab scale half-cell shown in Figure 1. Instead of the anode and cathode shown in the Figure 1, SS304 plates (Goodfellow Corporation) were used on both the sides. LiAlO₂ separator containing (Li₀.₆₂K₀.₃₈)₂CO₃ was used as the separator matrix. Oxidant gas with a composition of 30% CO₂ and 70% air was passed on both the ends. A gold reference electrode with a reference gas of 66%CO₂ and 33% O₂ was connected through a salt bridge.

Scanning electron microscope (SEM) was used to study the microstructure of the SS304, Co-Ni coated SS304 and the separators collected from 3 cm² cells. Energy dispersive spectroscopy (EDAX) was employed to investigate the composition of the corrosion scales formed in case of bare and surface modified SS304 electrodes in the presence of cathode gas.
conditions. LiAlO$_2$ separators were taken after the experiment and were analyzed for Cr content using EDAX.

**Results and discussion**

*Stability tests:* - Before studying the electrochemical performance of bare and surface modified SS 304, stability tests have to be performed to make certain that the developed coatings sustain the molten carbonate environment and that they offer beneficial protection to the substrate. Stability of the coating was ascertained by immersion tests and morphological and compositional analysis of the molten carbonate melt, SS samples, and the LiAlO$_2$ separators. It is well known that stainless steel forms complex corrosion products [12,17] in the carbonate melt. The composition of these corrosion products depends on the constituents and surface composition of the steel. Some of these corrosion products (like LiCr$_2$O$_4$, NiO etc) are not stable in the molten carbonate and dissolve in the melt. Therefore it is important to analyze the melt for dissolved concentrations of SS constituent elements.

*Atomic absorption spectroscopy:* - The short-term stability of the corrosion products formed in case of SS304 and Co-Ni-SS304 in molten carbonate eutectic were determined using immersion tests. Atomic absorption spectroscopy (AAS) was used to analyze the dissolved chromium and nickel in the melt. Figure 2 shows the results of AAS analysis for the dissolved chromium and nickel in the carbonate melt as a function of time. As shown in the plot, the concentration of chromium in the melt was about three times higher in case of bare SS304 when compared to that of Co-Ni-SS304. Molar concentration of nickel was also significantly higher for the case of bare SS304 when compared to the surface modified SS304. These results indicated that surface modification leads to the formation of more resistive corrosion scales that are resistant to Cr dissolution in the molten carbonate environment. The amount of nickel and chromium cations in the carbonate melt increases with time and saturates after about 100 hours. Biedenkopf *et al.* [20] report increased concentration of Cr with time in the melt for high alloy steels. Further, they also observed that the oxide film thickness varied inversely with the chromium content in the steel. The thinner oxide scale for higher Cr content was attributed to active dissolution of Cr in the melt. This agrees with the results reported here and shows that coating Co-Ni alloys reduces the Cr dissolution, thereby leading to the formation of a stable oxide. Previous investigators have also reported coloring of the melt (melt color changes to yellow) due to chromium dissolution.
Coloring of the melt due to chromium dissolution was observed in our case also at the end of the experiment. However, the coloring was more in case of SS304 when compared to that of Co-Ni-SS304.

**SEM and EDAX analysis:** - SEM and EDAX were used to identify the morphology and compositional changes in the bare and surface modified SS304 with exposure to molten carbonate. Analyses were carried out on SS304 and Co-Ni-SS304 taken out of 3 cm² cells after 500 hours of operation under cathode gas conditions. Compositional and morphological analysis of fresh SS304 and Co-Ni-SS304 were also done for comparison. Figure 3 shows the scanning electron micrographs of fresh and post test SS304 and Co-Ni-SS304 samples. Electroless deposition leads to the formation of amorphous films of Co-Ni on top of the SS304. These amorphous coatings influence the composition and morphology of the corrosion scales to a great extent. In the case of post test SS304, cubic crystals are seen to uniformly cover the whole surface, while in the case of Co-Ni-SS304; the corrosion scale is more undefined. EDAX analysis on the corrosion scale of SS304 indicates the presence of iron (Figure 4). It has been shown in literature that SS304 forms a corrosion layer consisting of LiFe₅O₈ [12] under cathode conditions. LiFe₅O₈ has a cubic spinel type crystal structure and is closely related to magnetite (Fe₃O₄) [20]. The oxide scale formed for various low and high alloy steels was investigated by Biedenkopf *et al.* [20]. They found that the oxide layer thickness increased with decrease in Cr content in the alloy. In general the oxide scale after 1000 hours of immersion varied from 10 µm to 500 µm for steels with 2% to 25% Cr respectively. In our case, the depth of penetration for the EDAX analysis is around 1 µm and this prevented assessing the entire corrosion scale. The relative composition data for fresh and post test SS304 are given along with the respective EDAX diagrams. The other interesting information that could be seen from the EDAX analysis in case of SS304 is the decrease in the chromium content on the corrosion scale. SS304 has a high initial Cr content (18 wt.%), which decreases with interaction in molten carbonate under cathode gas conditions. This is clearly due to the dissolution of chromium into the electrolyte through oxidation and disintegration. In case of Co-Ni-SS304, EDAX analysis indicates a high Co and Ni content in the scale. The cobalt and nickel content did not change appreciably except for the inclusion of potassium in the corrosion scale (also seen in SS304).

X-ray diffraction analysis was carried out on the corrosion scales formed on the stainless steel samples in order to gain further understanding of the corrosion products that are formed
during the interaction of steel with the molten carbonate under cathode gas conditions. Figure 5 shows the X-ray patterns obtained in case of posttest SS304 and Co-Ni-SS304. The diffraction pattern differed significantly in case of SS304 and Co-Ni-SS304 suggesting the presence of different compounds on the surface. The irregularity of the surface of the corrosion scale lead to a lot of disturbance in the X-ray pattern. In case of SS304, the surface was covered with mixed iron oxides like LiFeO$_2$ and LiFe$_5$O$_8$. Chromium oxides were absent which agrees with the EDAX analysis results. In case of Co-Ni-SS304, lithiated cobalt oxides and mixed nickel-cobalt-iron oxides covered the surface. Lithiated Co and Ni oxides are quite stable and offer good barrier protection under MCFC cathode conditions. Since microencapsulation gives rise to more uniform and layered deposits, the barrier properties can be expected to be superior compared to the conventional methods of electro cladding and electrodeposition. This is evident from the AAS data, which shows the decrease in the Cr content in the melt in case of Co-Ni-SS304 when compared to SS304.

The corrosion products that are unstable in the molten carbonate can undergo disintegration and get included in the adjacent electrode material. This can sometimes alter the porosity of the material leading to lowering of performance. In our experimental conditions, we placed the LiAlO$_2$ separator in direct contact with the SS304 and Co-Ni-SS304 plates. AAS studies showed the presence of chromium in the melt in case of SS304 and Co-Ni-SS304. This could be due to the disintegration of Cr based corrosion products formed during oxidation of SS304. We attempted to do SEM and EDAX analyses of the LiAlO$_2$ separator after the experiment was done in order to find out the morphological and compositional changes in the separator due to the corrosion reactions happening on the adjacent current collector. Figure 6 shows the SEM micrographs of fresh and used (Posttest from SS304 and Co-Ni-SS304 containing 3cm$^2$ cells) LiAlO$_2$ separators. The morphology of post test LiAlO$_2$ does not differ significantly from fresh one except for the apparent decrease in void area, which could be because of the electrolyte filling. In case of post test LiAlO$_2$ taken from cells containing SS304, presence of small flake like corrosion products was observed. Spot analysis by EDAX showed high chromium content in these corrosion products. EDAX analysis on the complete LiAlO$_2$ separator shows an average chromium concentration of 6.5% in case of SS304. The amount of Cr present in the case of Co-Ni-SS304 was found to be 0.24%.
Cyclic voltammetric studies: - Figure 7 shows CVs done on SS304 and Co-Ni-SS304 after 2 h of immersion in the Li/K carbonate melt purged with cathode gas. The potential scan began at a rate of 10 mV/s from –1.6 V in the anodic direction and reversed direction at 0 V to reach –1.6 V. This region covered all the oxidation and reduction processes happening in MCFC under different operating conditions.

The corrosion behavior of 304 stainless steel could be expected to be very complex because of the large number of components comprising the steel and because it can form multiple corrosion layers with mixed compositions. The relatively high current observed at potential of –1.6 V in case of bare and surface modified SS 304 during the start of the forward scan can be attributed to the carbon precipitation that occurs due to the decomposition of carbonate eutectic [12,22-23]. Further increase in the potential in the anodic direction leads to peak formation in case of SS304 at around –1.2 V. Keijer et al [12] observed a similar peak in their study of SS304 under cathode gas and attributed it to the formation of FeO by oxidation of surface Fe. This peak was absent in case of Co-Ni-SS304, which could be explained by the absence of Fe on the surface for oxidation.

On continuing the potential scan in the anodic direction, an increase in current followed by a plateau is observed at around –0.8 V in the case of SS304. In the case of Co-Ni-SS304, the current increases slowly and no definite peak was observed. This increase in current can be ascribed to the oxidation of Ni to NiO and to dissolved nickel ions. In case of iron rich scale, the current is mainly due to the oxidation of surface iron oxides to LiFeO₂. Based on the high concentration of nickel and cobalt in case of surface modified SS304, one can expect more contribution to the anodic current to come from the nickel and cobalt oxidation. Similar results have been reported in the literature [17].

As the anodic scan is continued, the oxidation current increases until 0 V in case of SS304. Peaks appear around –0.1 V in case of Co-Ni-SS304. The contributions to this current come from formation of LiFe₅O₈, trivalent nickel and cobalt ions and chromate ions [17,23]. In case of Co-Ni-SS304, the contribution coming from oxidation of bivalent nickel and cobalt ions becomes significant. This oxidation process starts at around –0.5 V or higher and happens simultaneously with the iron oxidation process. Vossen et al [17] found out the presence of trivalent nickel using XRD analysis. With the formation of these trivalent nickel ions, vacancies are introduced into the lattice, which subsequently improved the ionic conductivity of the scale.
Oxidation of chromium happens at more positive potentials of –0.3 V or higher. Li$_2$CrO$_4$ is a thermodynamically stable product, but is not stable as a corrosion layer and dissolves as chromate ions. Vossen et al [14] observed a current increase at –0.3 in their study with pure chromium and observed coloring of the melt due to the presence of dissolved chromium. The dissolution currents observed in case of pure chromium was higher than other alloys. In case of pure chromium, lithium chromite is readily available at the electrode-electrolyte interface so that the chromate ions can form easily and dissolve into the melt. In case of stainless steel and surface modified alloys, the oxide scale is more complex than that of pure chromium. This is due to the presence of other type of oxides, which could cause transport problems and thus decrease the formation and dissolution of chromate ions. Therefore amount of chromium dissolved in the melt is a clear indication of the integrity of the passive layer formed. Further increase in the potential leads to anodic decomposition of molten carbonate [12].

In the cathodic scan, an increase in current could be observed starting from around –0.5 V. This phenomenon was observed for both bare and surface modified SS 304. This increase in current corresponds to the reduction of trivalent nickel ions in the oxide scale. The reduction of chromate ions also proceeds at the same potential. Further increase of the potential in the cathodic direction to –0.9 V leads to the reduction of $\alpha$-LiFe$_5$O$_8$ to LiFeO$_2$ and then to FeO. Nickel oxide also reduces to metallic Ni at this potential.

**Corrosion studies under open circuit conditions:** At open circuit conditions, the potential of bare and surface modified SS 304 changes with increased exposure times from –1 V to the potential of oxygen reduction reaction. The rate of oxidation depends on the amount of oxidant gas the samples are exposed to. In this case, since the samples were immersed in a melt of molten carbonate through which oxidant was purged, the rate of oxidation will be slower than in the real case where the bipolar plates and current collectors are flooded with oxidant gas. This potential change as shown in Figure 8 is a multi-step process based on the different oxidation reactions happening at the surface. The open circuit profile traced in case of surface modified SS 304 is seen to be different than that of bare SS 304 suggesting the different nature of the corrosion scale. Surface composition of the alloy strongly determines the nature of the potential change. Formation of a passive layer is a nucleation and growth process. The complexity of this passive layer strongly depends on the surface composition of the alloy. In the potential range of interest namely –1.0 V to 0.0 V, iron gets oxidized to FeO, LiFeO$_2$ and LiFe$_5$O$_8$, nickel and
cobalt to lithiated NiO and chromium to LiCrO\textsubscript{2} and Li\textsubscript{2}CrO\textsubscript{4}. The different corrosion reactions and associated products in this potential range were elaborated in the cyclic voltammogram studies. The first potential shift under cathode gas conditions is due to the surface oxidation of the sample. This layer mostly comprises of oxides of chromium and nickel in case of SS304. Nickel oxides and cobalt oxides can be expected to form in case of Co-Ni-SS304. Chromium oxidizes react with Li\textsubscript{2}CO\textsubscript{3} from the electrolyte to form a layer of LiCr\textsubscript{2}O\textsubscript{4} that dissolves slowly into the melt thereby coloring the melt [14]. These initial layers are highly porous in nature and lead to the slow oxidation and convert the underlying Fe to LiFe\textsubscript{5}O\textsubscript{8}. This phenomenon causes the second potential shift observed in open circuit plot of SS304. At the end of this potential change, the corrosion scale consists of outer porous lithium ferrite layer (LiFe\textsubscript{5}O\textsubscript{8}) with inner layers containing dense chromium oxides that prevents the external diffusion of other metal ions thereby checking the growth of external ferrite layer. In case of Co-Ni-SS304, the corrosion scale is made of outer CoO-NiO layers that could cover the LiFe\textsubscript{5}O\textsubscript{8} and chromium oxide inner layers. This also explains the observed decrease in chromium dissolution rate when the SS304 samples were coated with Co-Ni.

**Tafel polarization studies:** To quantify the redox reactions happening on the surface of the current collector, Tafel extrapolation from potentiodynamic curves were measured between OCP ± 250 mV at different temperatures both in the presence and absence of the oxidant gas. Tafel polarization studies were carried out in a three-electrode 3-cm\textsuperscript{2}-lab scale cell containing SS304 and Co-Ni-SS304 electrodes as the working and counter electrodes. Gold (oxygen reduction) served as a reference electrode. The electrodes were separated by a LiAlO\textsubscript{2} ceramic tile containing Li/K carbonate melt (62-38mol\%). The cell is connected to a gold/oxygen reference electrode through a salt bridge. The potential was scanned at a rate of 25 mV/s. Figure 9 compares the Tafel polarization curves obtained for SS304 under different gas and temperature conditions. In the presence of cathode gas, the electrode potential was seen to be close to 0 V (vs. Au/[2CO\textsubscript{2}+1O\textsubscript{2}]) indicating that the potential is governed by the oxygen reduction reaction. In the absence of gas, the potentials shift to – 0.25 V (vs. Au/[2CO\textsubscript{2}+1O\textsubscript{2}]), which is the mixed potential of the various metal oxides present on the corrosion scale. The high scan rate ensured minimum changes on the surface. During the anodic scan the oxidation of the O\textsuperscript{2−} species happens along with the oxidation of metal to metal oxide. Figure 10 shows the Tafel polarization curves obtained for Co-Ni-SS304 under similar conditions. The potentiodynamic
curves were very similar to the case of SS304 except for the difference in magnitude of the oxidation and reduction currents. In case of Co-Ni-SS304, both the cathodic and anodic currents were larger than the corresponding currents in case of SS304. This indicates that the oxygen reduction reaction, which contributes predominantly to the observed currents in the Tafel polarization curves, occurs at a faster rate in the Co-Ni-SS304 substrate. This can be expected because Co-Ni-SS304 forms a CoO-NiO rich corrosion scale that has a higher exchange current density for oxygen reduction reaction when compared to that of LiFeO₂ and LiFe₅O₈, which forms the corrosion scale on SS304.

Effect of corrosion scales on electrolyte management: - Electrode reaction takes place mainly near the meniscus (three phase boundary) where the mass transfer resistance is least for the gas diffusing through liquid to the reaction surface. Electrolyte distribution therefore significantly affects the performance characteristics of the electrodes. As observed by previous investigators, the presence of Cr in the alloy leads to a continuous dissolution of chromate ions into the melt. This dissolution is accompanied by an unwanted side reaction, which consumes the electrolyte. Therefore, apart from the loss of electrolyte due to the reaction of chromium (from SS) with Li₂CO₃, the continuous oxide formation can also be expected to compromise the electrolyte management thereby affecting the performance of the electrode. Coating SS304 with Co-Ni reduces the Cr dissolution and thereby eliminates the unwanted side reaction.

The whole surface of SS 304 has well-formed crystals of cubic spinel type LiFe₅O₈. On the other hand Co-Ni modified SS 304 can be expected to have a layers of CoO-NiO above the layers of LiFeO₂. Figure 11 shows a schematic of how a corroded SS 304 bipolar plate will look like under MCFC cathode conditions. The porous MCFC cathode is shown here to be completely wetted by the electrolyte and the porous corrosion scale derives electrolyte by capillary action. Since the oxidant is being passed through the bipolar plates, oxygen reduction reactions can partly take place in the pore walls of corrosion scales on the current collector. In order to understand better the reactions occurring on SS304 and Co-Ni-SS304 under MCFC conditions, impedance measurements were carried out as a function of different gas compositions and temperatures.

Electrochemical Impedance Spectroscopy (EIS) studies: -EIS analysis was carried out using the same electrochemical set up described in the Tafel polarization studies. EIS analysis was performed at equilibrium potential (open circuit) on the SS304 and Co-Ni-SS304 electrodes in
the presence and absence of gas. Figure 12 shows the impedance analysis of SS304 electrode at different temperatures and gas conditions. The impedance response at any given temperature is characterized by the presence of two arcs. The high frequency arc has a slope of 0.5 that could be representative of the conductivity of the porous electrode. The low frequency loop indicates the complex charge transfer and mass transfer controlled reactions happening on the surface of the corrosion scale. The oxygen reduction reaction predominates at the electrode surface in the presence of oxidant. When the gas supply is cut off, the oxygen reduction reaction still proceeds on the surface depending upon the availability of dissolved oxygen in the melt. However, the extent of this reaction is small owing to the decreased availability of oxygen, which in turn causes the potential to shift to that of metal oxide value. The polarization impedance begins to decrease gradually with time when the gas is cut off before stabilizing after about 4 hours. The impedance response followed a similar trend at higher temperatures. However the magnitude of the polarization resistances for surface reactions decreased considerably. This can be expected due to the dependence of the activation energy of the reactions on the temperature. The conductivity of the porous scale is also seen to increase at higher temperatures.

Figure 13 shows the impedance response of Co-Ni-SS304 electrode as a function of different gas compositions at three different temperatures. The impedance responses are very similar to the ones obtained in case of SS304 except for the difference in magnitude. Co-Ni encapsulation on SS304 leads to the formation of CoO-NiO rich corrosion scales on the surface of the modified current collector. CoO-NiO has a higher exchange current density for oxygen reduction reaction when compared to that of LiFeO₂. Therefore a smaller polarization resistance is seen in case of surface modified SS304 when compared to that of bare SS304. This explains the observed decrease in impedance in case of surface modified SS304 when compared to that of SS304. Temperature also has a similar influence like in the case of bare SS304 wherein the magnitude of polarization resistance decreases with increase in temperature.

Careful examination of these impedance curves suggests that the loops, which are seen in both cases of Co-Ni-SS304 and SS304, are either depressed semicircles or arcs of semicircles whose center is displaced from the real axis. The data can be compared with the impedance of a plausible electrical equivalent circuit by complex non linear least squares fitting (CNLS) to extract parameters (circuit elements) which can be related to physical processes. Although we usually employ ideal resistors, capacitors and inductances in an equivalent circuit, actual real
elements only approximate ideality over a limited frequency range. Like in our case, the impedance loops are present as depressed semicircles signifying deviation from ideality. To compensate for this deviation from reality, a distributed phase element was added to the equivalent circuit. Figure 14a shows the electrical equivalent circuit that was used to fit the experimental impedance data obtained for the case of SS304 and Co-Ni-SS304. The distributed element used in the equivalent circuit is a \textit{Zarc-Cole} type wherein a constant phase element (CPE - signifies the semi-infinite non-uniform diffusion occurring in a porous electrode), is placed in parallel with an ideal resistor (reaction resistance). The \textit{Zarc} produces a complex plane curve, which forms an arc of a circle with center, displaced from the real axis. Further details about the \textit{Zarc-Cole} fitting and CPE can be obtained from literature [24]. Figure 14b shows the comparison between experimental data and equivalent circuit fitting. The experimental data is shown as dots and the solid line represents the model fit. The parameter polarization resistance, \( R_2 \), which is extracted from the impedance response using the equivalent circuit model, is plotted as a function of time for both the Co-Ni-SS304 and SS304. The negative value in the time axis denotes the point when the impedance response was evaluated in the presence of gas. At time = 0 h, the gas was cut off and the impedance analysis was carried out at different intervals of time. The polarization resistance in the presence of oxidant is significantly lower in case of Co-Ni-SS304 (22.86 \( \Omega \)) when compared to SS304 (120.68 \( \Omega \)). This can be expected because of the poor kinetics for oxygen reduction on LiFeO\textsubscript{2} substrate when compared to CoO-NiO. When the gas is cut off, the observed polarization resistance is governed by mixed reactions happening at the surface including the oxygen reduction reaction that happens at a lower extent. The resistance \( R_1 \) denoting the conductivity of the porous electrode remained more or less constant irrespective of the gas conditions. \( R_1 \) obtained for SS304 at 650\degree C using the equivalent circuit model varied between 5.71 \( \Omega \) and 5.29 \( \Omega \) while it varied between 1.32 \( \Omega \) and 1.28 \( \Omega \) for the case of Co-NiO-SS304. This shows that the corrosion scale formed in case of Co-Ni-SS304 has a higher conductivity when compared to that formed on SS304. The polarization resistance \( R_2 \) and ohmic resistance \( R_1 \) at 700\degree C and 750\degree C followed similar trend like in the case of 650\degree C even though the magnitude was significantly lower at higher temperatures suggesting improved kinetics and better conductivity.

\textit{Polarization plots:} - Current-potential plots were obtained on SS304 and Co-Ni-SS304 at 650\degree C under oxidant gas conditions. The current was varied from 0 to 5 mA/cm\textsuperscript{2} and the potential
change (IR corrected) was measured with respect to the gold reference electrode. The slope of the linear part of i-V curve was taken as the polarization resistance ($R_p$). Figure 15 shows the i-V plots obtained for SS304 and Co-Ni-SS304 at 650°C. $R_p$ calculated based on this method showed a value of 22 Ω for the case of Co-Ni-SS304 and 80 Ω for SS304. These values seem to agree with the trend predicted by the impedance analysis. The lower polarization in case of Co-Ni-SS304 is obviously due to the presence of CoO-NiO on the surface, which shows better kinetics for oxygen reduction reaction compared to LiFeO$_2$, which is seen on the surface of SS304.

**Conclusions**

Surface modification of SS 304 was carried out by electroless plating of monolayers of nanostructured Co-Ni. Immersion tests that were carried out on SS304 and Co-Ni-SS304 indicated more chromium dissolution in case of SS304 when compared to Co-Ni-SS304. SEM and EDAX analysis of the post test SS304 indicated a loss of Cr from the surface. The surface composition of Co-Ni-SS304 showed very little change in terms of Co and Ni content suggesting that the corrosion scale predominantly consists of Co and Ni oxides. XRD patterns of the corrosion scales indicated the presence of lithium ferrite along with LiFe$_5$O$_8$ in case of SS304 and mixed lithium-cobalt-nickel-iron oxides in case of Co-Ni-SS304. The open circuit potential response of the SS304 and Co-Ni-SS304 measured as a function of the exposure time showed the presence of several plateaus due to the different corrosion reactions happening on the surface of the sample. Cyclic voltammograms were used as a qualitative technique to compare the effect of surface modification on these corrosion reactions and it was seen that the currents due to formation of scale were significantly lower in case of surface modified SS 304 when compared to bare steel. Tafel polarization and impedance spectroscopic studies were done on SS304 and Co-Ni-SS304 samples placed in contact with LiAlO$_2$ separator containing molten Li/K carbonate electrolyte under different gas conditions and temperatures. The open circuit potential changed from 0V under cathode gas to −0.25 V when the gas supply was turned off. Oxygen reduction reaction predominates the cathodic reaction in the presence of oxidant. In the absence of gas, the cathodic reaction comprised of reduction of metal oxides and the dissolved oxygen. Complex impedance responses were obtained as a function of gas condition and temperature for SS304 and Co-Ni-SS304. The impedance responses were fitted using a Zarc-Cole type equivalent
circuit and parameters like polarization resistance and conductivity of corrosion scales were obtained. Conductivity of the corrosion scale was higher in case of Co-Ni-SS304 when compared to SS304. Polarization resistance for oxygen reduction was significantly lower in case of Co-Ni-SS304 when compared to SS304, which could be due to the presence of CoO and NiO on the surface as compared to LiFeO₂ in case of SS304. Polarization resistance values estimated from complex impedance plots agreed with those obtained using i-V plots.
References


Figure 1. Schematic diagram of a 3-cm²-electrochemical fuel cell. Au/(2CO₂+1O₂) reference electrode with a salt bridge was used for measuring cathode and anode potential during polarization studies.
Figure 2. Atomic absorption spectroscopy analysis of dissolved chromium (a, top) and nickel (b, bottom) concentrations in the molten carbonate melt due to the immersion of SS304 and Co-Ni-SS304.
Figure 3. SEM photographs of fresh and post-test SS304 and Co-Ni-SS304. Post-test specimens were obtained after 500 hours of operation in molten carbonate under cathode gas conditions.
Figure 4. EDAX analysis of fresh and post test SS304 and Co-Ni-SS304. Post test specimens were obtained after 500 hours of operation in molten carbonate under cathode gas conditions.
Figure 5. X-ray diffraction patterns of corrosion scales formed in posttest SS304 and Co-Ni-SS304. Posttest specimens were obtained after 500 hours of operation in molten carbonate under cathode gas conditions.
Figure 6. SEM photographs of fresh and posttest LiAlO\textsubscript{2} separators used in cells containing SS304 and Co-Ni-SS304. Posttest specimens were obtained after 500 hours of operation in molten carbonate under cathode gas conditions.
Figure 7. Cyclic voltammograms of SS304 and Co-Ni-SS304 recorded after 2 hours of immersion in molten carbonate at open circuit potential under cathode gas conditions.
Figure 8. Open circuit potential response of SS304 and Co-Ni-SS304 as a function of exposure time in molten carbonate melt under cathode gas conditions. The potential is referenced to a gold electrode with 2CO₂+1O₂ as the reference gas.
Figure 9. Tafel polarization curves for SS304 obtained as a function of different gas compositions and temperatures. The potential is referenced to a gold electrode with 2CO₂+1O₂ as the reference gas.
Figure 10. Tafel polarization curves for Co-Ni-SS304 obtained as a function of different gas compositions and temperatures. The potential is referenced to a gold electrode with $2\text{CO}_2+\text{1O}_2$ as the reference gas.
Figure 11. Schematic of an oxidized SS304 electrode in contact with a porous cathode in a molten carbonate fuel cell.
Figure 12. Nyquist plots of impedance response of SS304 obtained as a function of different gas compositions and temperatures.
Figure 13. Nyquist plots of impedance response of Co-Ni-SS304 obtained as a function of different gas compositions and temperatures.
Figure 14a. Schematic of the electrical equivalent circuit that was used to fit the experimental impedance response obtained for the cases of SS304 and Co-Ni-SS304.
Figure 14b. Comparison of equivalent circuit fitting results with the experimental data for the case of Co-Ni-SS304 at 700°C.
Figure 15. Comparison of polarization behavior of SS304 and Co-Ni-SS304 at different current loads.