

A study of a corrosion-resistant coating for a separator for a molten carbonate fuel cell

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Abstract

The corrosion behaviour of nickel and copper coatings in the current-collector area of separators and a Ni/Al intermetallic compound coating in the wet-seal area of separators for molten carbonate fuel cells is evaluated under immersion in molten carbonate salt. The corrosion-protection effect of nickel and copper coatings on 316L stainless steel is evaluated in an electrochemical half-cell by means of a potentiostatic polarization technique. In addition, the corrosion-protection behaviour of a nickel-coated layer in the anode current-collector area and a Ni/Al-coated layer in the wet-seal area of the separator are studied during operation of a single cell for 10 days. Nickel suffers no observable corrosive attack for up to 500 h in the anode gas atmosphere (H_2/CO_2). By contrast, nickel and copper exhibit less corrosion resistance than 316L stainless-steel during exposure to the cathode gas atmosphere (CO_2/O_2). Under a potentiostatic anodic polarization of -1.0 V (versus $CO_2/O_2/Au$), nickel-coated 316L stainless-steel displays a lower anodic current density than copper-coated and uncoated 316L stainless-steel. NiAl with a high melting point has better corrosion resistance than other Ni/Al intermetallic compounds. From single cell tests, it is found that nickel and NiAl coatings are efficient for the protection of stainless-steel in the anode area and wet-seal area, respectively. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The molten carbonate fuel cell (MCFC) generates electricity directly through an electrochemical reaction between hydrogen and oxygen and, therefore, has high electrical efficiency [1–4]. At the same time, its impact on the environment is minimal. This is a co-generation system for electricity and heat supply that is capable of supplying energy in the form of heat by using the recovered thermal energy from the generation process. Suitable fuels include coal gas, LPG, methanol, and even natural gas. To be economically competitive and commercially viable, the cells and cell stacks should have long life times, about 40 000 h is recommended [5]. Unfortunately, the lifetime of state-of-the-art sub-scale and full-scale stacks falls short of this target, only in a few tests does it approach or exceed the 10 000 h mark.

One of the major material problems in MCFCs is the corrosion of the metal separator plate. A typical

corrosion-resistant separator may consist of nickel or a nickel-copper alloy coating on stainless-steel in the anode gas atmosphere (H_2/CO_2), and iron or nickel-based alloy in the cathode gas atmosphere (CO_2/O_2) [6].

The high costs of separators in the present design are basically due to the expensive processes of cladding or coating to fabricate a composite layer for the corrosion-resistant material of anode. Nickel coating by various techniques has been considered as an alternate, cheaper process than nickel cladding. Most of the coating processes studied to date, however, do not readily result in a defect-free coating at a competitive price, and coating defects such as cracks, pin holes, poor adherence, etc., have been found to degrade both the substrate and the coating.

Nickel-based high-temperature alloys are sufficiently corrosion-resistant for the cathode, but are not feasible for commercial use due to their high costs. Fe–Cr ferritic stainless-steel is low in cost, but it is not adequately corrosion-resistant. Fe–Ni–Cr austenitic stainless-steel is currently considered as a promising coating material for the cathode due to its good corrosion resistance and reasonable cost.

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A wet-seal technique has been widely applied for gas-sealing and retention of the molten carbonate electrolyte in MCFCs [7–9]. Since the wet-seal area is exposed to a severe corrosion environment, the cell performance is influenced by the corrosion resistance of wet-seal materials. The wet-seal simultaneously experiences reducing and oxidizing environments; only aluminum-containing alloys possess sufficient corrosion resistance under such environments. Aluminizing has generally been selected as the technique for enhancing the surface aluminum content for protection [10], and can be achieved by painting, thermal spraying or vacuum deposition, followed by diffusion heat treatment. According to Yuh et al. [11], the aluminized coating is expected to be sufficient for 40000 h of use provided that a coating of consistent quality is used. Research and development is now focusing on various aluminizing processes which will give a cost reduction and good adhesion.

It is well known that aluminizing treatment of the surface of nickel and nickel-base superalloys improves their oxidation resistance at high temperature. The intermetallic phases of NiAl₃, Ni₂Al₃ and NiAl in the Ni–Al binary system play important roles in maintaining the oxidation resistance of superalloys, and Ni₃Al is the principal strengthening phase of nickel-base superalloys. Numerous studies had been made on the hot corrosion of Ni/Al intermetallic compounds in oxidizing atmospheres (for examples, oxygen, air, CO₂–CO, H₂O–H₂, H₂–O₂ etc.), whereas there are few corrosion data for Ni/Al compounds in molten carbonate salts.

In this study, the corrosion behaviour of Ni, Cu and 316L stainless-steel is compared thermodynamically under immersion conditions in the anode and cathode gas atmospheres of a MCFC. The deposition of Ni and Cu on 316L stainless-steel is electroplating method which is an easy and low-cost process. NiAl was selectively deposited on the wet-seal area of a single cell by means of electroplating and a physical vapour deposition method. The corrosion-protection effect of Ni and Cu coatings on the 316L stainless-steel is evaluated under conditions which simulate the anode in a MCFC. In addition, the corrosion-protection behaviour of a nickel coating layer in the anode current-collector area and a NiAl coating layer in the wet-seal area of the separator is evaluated in a single cell for 10 days.

2. Experimental

2.1. Ni and Cu coatings on 316L stainless-steel

Ni and Cu coatings were electroplated from a Watts nickel bath and a copper sulfate bath, respectively. The substrate was degreased in alkaline solution at 323 K and lightly etched with HCl solution immediately before plat-

ing. For nickel coating, Woods nickel strike plating was introduced to increase the adhesion before nickel plating in the Watts bath.

2.2. NiAl coating on the single cell

The NiAl phase on the stainless-steel substrate was formed by pre-coating of nickel and plating with Al, then heat-treating at 1073 K for 3 h in a H₂/N₂ gas atmosphere. The nickel-coated layer was formed by electroplating in the Watts bath. After heat treatment, the structure of the Ni/Al coating layer was examined by SEM, EDS and XRD analysis.

2.3. Corrosion test during operation of a single cell

The single cell of a MCFC consisted of an anode, a separator (or current collector), green electrolyte tape, green carbonate mixture tape, and the cell frame. The anode and the cathode were Ni–10 wt.% Cr porous plaque and in situ oxidized NiO porous plaque, respectively. The anode current-collector was made from nickel-coated 316L stainless-steel and compared with one of 316L stainless-steel. The cathode current-collector and cell frame were made from 316L stainless-steel. The cell also contained a green electrolyte tape of 40 wt.% LiAlO₂ and green electrolyte of 60 wt.% carbonate mixture (62 mol.% Li₂CO₃–38 mol.% K₂CO₃). The anode and cathode gases were 80% H₂–20% CO₂ and 67% CO₂–33% O₂, respectively. The cell was operated under a load of 100 mA cm⁻² and a cell voltage of 0.7 ± 0.02 V for 10 days. After operating of the cell, the oxide layers of the current-collector and wet-seal area were examined by SEM and EDS analysis.

3. Results and discussion

3.1. Corrosion in anode / cathode gas atmosphere

The reactions which occur in molten carbonate salt at the anode gas and the cathode gas atmospheres are as follows:

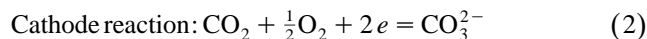
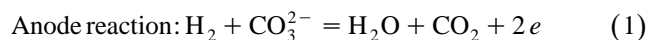


Table 1
Equilibrium potentials of anode and cathode reactions (vs. CO₂/O₂/Au) at 923 K [12]

| Reaction | Equilibrium potential (V) | Compositions of gases |
|----------|---------------------------|--|
| Anode | –1.138 | P _{CO₂} /P _{H₂} /P _{H₂O} = 0.15/0.75/0.15 |
| Cathode | –0.041 | P _{CO₂} /P _{O₂} /P _{H₂O} = 0.335/0.165/0.028 |

Table 2

Equilibrium potentials for oxidation of various metals (vs. $\text{CO}_2/\text{O}_2/\text{Au}$) at 923 K [12]

| Reaction | Equilibrium potential (V) | |
|--|---------------------------|-------------|
| | Anode gas | Cathode gas |
| $\text{Ni} + 1/2\text{O}_2 = \text{NiO}$ | -0.872 | -0.840 |
| $2\text{Cu} + 1/2\text{O}_2 = \text{Cu}_2\text{O}$ | -0.595 | -0.563 |
| $\text{Fe} + 1/2\text{O}_2 = \text{FeO}$ | -1.122 | -1.090 |
| $2\text{Cr} + 3/2\text{O}_2 = \text{Cr}_2\text{O}_3$ | -1.684 | -1.673 |

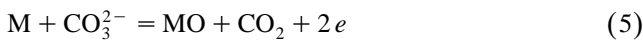
The equilibrium potentials of these reactions can be obtained by the Nernst equation.

$$E = E^\circ(\text{H}_2\text{O}, \text{CO}_2/\text{H}_2, \text{CO}_3^{2-}) - \frac{RT}{2F} \ln \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}} \cdot p_{\text{CO}_2}} \quad (3)$$

$$E = E^\circ(\text{CO}_2, \text{O}_2/\text{CO}_3^{2-}) - \frac{RT}{2F} \ln \frac{1}{p_{\text{CO}_2} \cdot p_{\text{O}_2}^{1/2}} \quad (4)$$

The equilibrium potentials at 923 K and the composition of gases used in the calculations are listed in Table 1 [12]. The equilibrium potentials for reactions (1) and (2) are about -1.138 V and -0.041 V, respectively, with respect to the reference electrode, 33% $\text{O}_2/67\%$ CO_2/Au .

The oxidation reaction of two-valent metals in molten carbonate salt can be represented by:



and the corresponding equilibrium potential is:

$$E = E^\circ(\text{MO}, \text{CO}_2/\text{M}, \text{CO}_3^{2-}) - \frac{RT}{2F} \ln \frac{a_{\text{M}} \cdot a_{\text{CO}_3^{2-}}}{a_{\text{MO}} \cdot p_{\text{CO}_2}} \quad (6)$$

Values for the equilibrium potential for the oxidation of various metals at 923 K in the anode and cathode gas atmospheres are listed in Table 2. In the anode gas atmosphere, the equilibrium potential for the oxidation of Ni and Cu is about -0.872 V and -0.595 V, respectively. By comparison with the data in Table 1, it can be seen that the equilibrium potentials for the oxidation of Ni and Cu

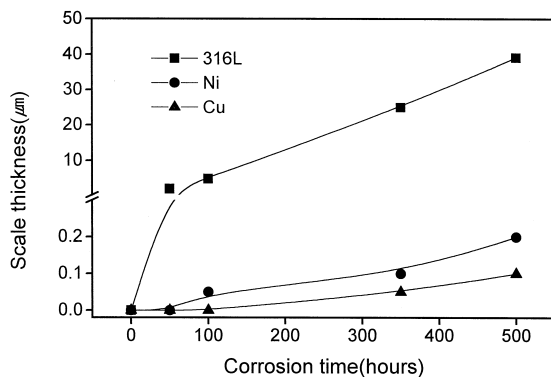


Fig. 1. Scale thickness variations of 316L, Ni and Cu with corrosion time in molten carbonate salt at 923 K and in a gas atmosphere (80% H_2 -20% CO_2).

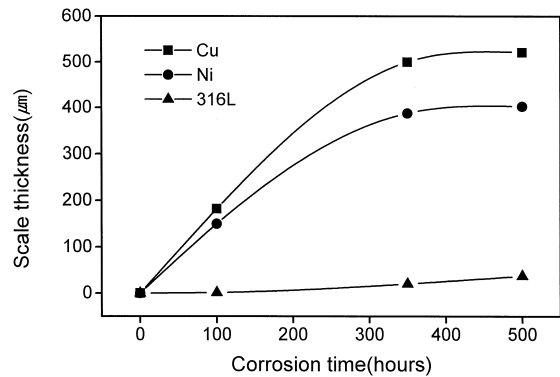


Fig. 2. Scale thickness variation of 316L, Ni and Cu with corrosion time in molten carbonate salt at 923 K in a cathode gas atmosphere (67% CO_2 -33% O_2).

are most positive than that of the anode reaction (1). Therefore, Ni and Cu are thermodynamically stable in the anode gas atmosphere. Because the equilibrium potential for the oxidation of Cr, which is the major alloying element of the 300-series stainless-steels, is more negative than that of the anode reaction (1), the corrosion of 316L stainless-steels will take place in the anode gas atmosphere.

Changes in the thickness of the oxide layer of 316L stainless-steel, Ni and Cu are presented in Fig. 1 as a function of the corrosion time (up to 500 h) in molten carbonate salt (62 m/o Li_2CO_3 -38 m/o K_2CO_3) at 923 K in the anode gas atmosphere (80% H_2 -20% CO_2). The oxide layer formed on the surface of 316L stainless-steels is very thick compared with Ni and Cu. In particular, nickel suffers no observable corrosive attack.

From Tables 1 and 2, it can be seen that the equilibrium potentials of Ni, Cu, Fe and Cr are more negative than that of cathode reaction (2). Thus, all the metals in Table 2 can corrode in the cathode gas atmosphere. According to Yuh et al. [11], the oxide layer formed on the surface of austenitic stainless-steels has a multi-layered structure and is compact in the cathode gas atmosphere. By contrast to the corrosion behaviour in the anode gas atmosphere, Ni and Cu exhibit less corrosion resistance than 316L stain-

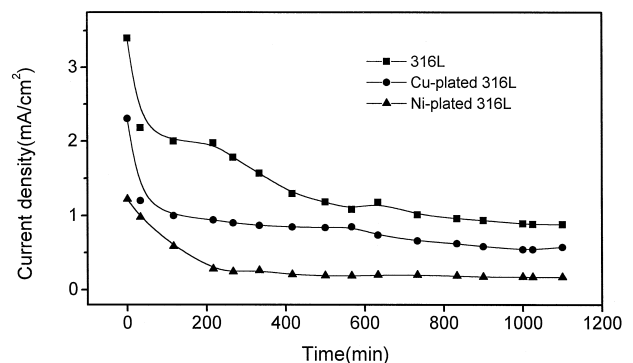


Fig. 3. Change of anodic current density with time in the molten carbonate salt at 923 K.

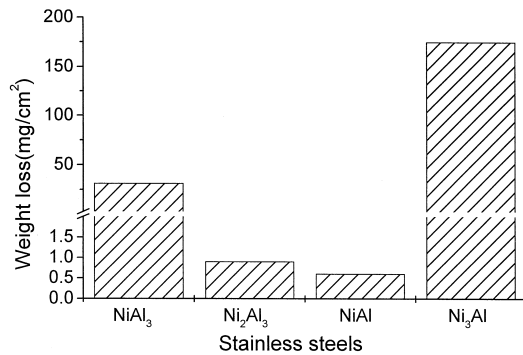


Fig. 4. Weight loss of Ni–Al intermetallic compounds corroded in molten carbonate salt at 923 K for 100 h.

less-steel during exposure to the cathode gas atmosphere (see Fig. 2). This is due to the lower potential of Ni and Cu with respect to that of the cathode reaction (2) and the formation of a porous oxide layer. Because a dense oxide layer can be formed on the 316L stainless-steel in the cathode gas atmosphere, stainless steel has a higher corrosion resistance than either Ni or Cu.

In order to evaluate the corrosion-protection effect of the nickel coating during operation of a MCFC, a corrosion test was performed for 1100 min under a potentiostatic anodic polarization of -1.0 V (versus $33\%O_2/67\%CO_2/Au$). Nickel-coated 316L stainless-steel displays

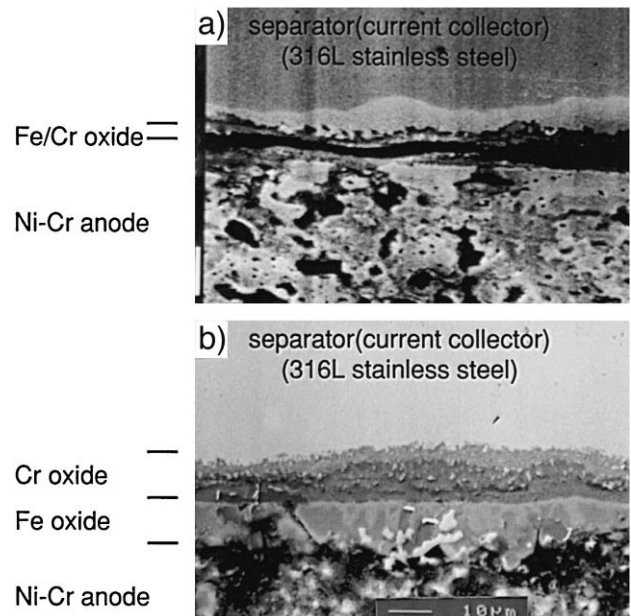


Fig. 6. Scanning electron micrographs of the current-collector/anode interface for: (a) Ni-coated 316L stainless-steel; (b) 316L stainless-steel. Tests in a single cell for 10 days at a current density of 100 mA cm^{-2} at 923 K.

a lower anodic current density than either Cu-coated or uncoated 316L stainless-steels Fig. 3. Thus, nickel is the optimum coating material in anode gas atmosphere.

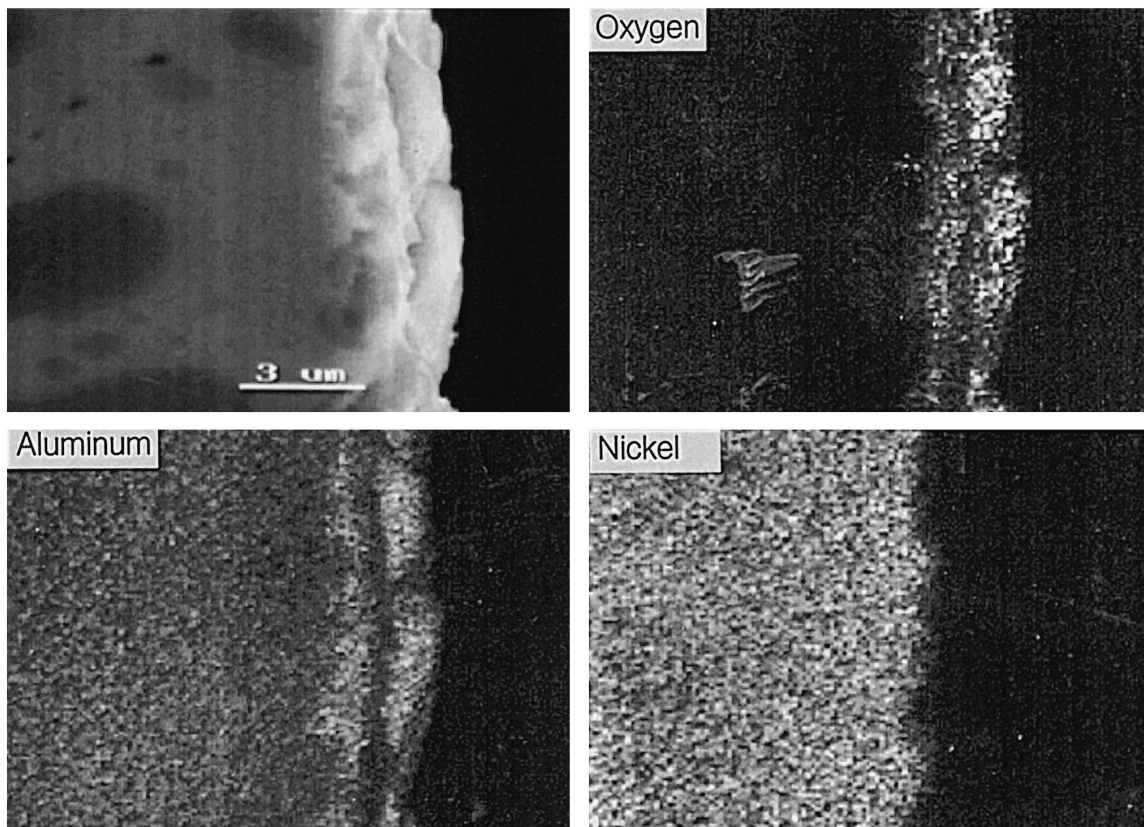


Fig. 5. Scanning-electron micrograph and mapping of elements in a cross-section of NiAl corroded in molten carbonate salt at 923 K for 100 h.

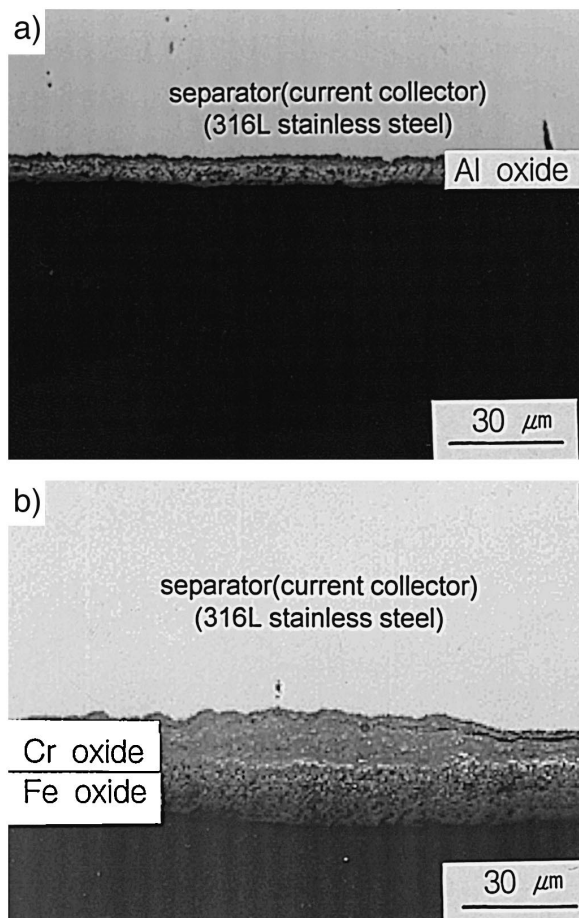


Fig. 7. Scanning electron micrographs of the cross-section of the wet-seal area after operation of a single cell for 10 days at a current density of 100 mA cm⁻² at 923 K: (a) NiAl-coated 316L stainless-steel; (b) 316L stainless-steel.

3.2. Corrosion of Ni/Al intermetallic compounds

In order to examine the corrosion resistance of Ni/Al intermetallic compounds in molten carbonate salt, an immersion test was performed for NiAl₃, Ni₂Al₃, NiAl and Ni₃Al prepared by an arc-melting method. The weight loss of Ni/Al intermetallic compounds corroded in molten carbonate salt (62 m/o Li₂CO₃–38 m/o K₂CO₃) at 923 K for 100 h is reported in Fig. 4. NiAl with a high melting point has better corrosion resistance than the other compounds. As shown in Fig. 5, it is considered that the good protection is due to the aluminum oxide formed on the surface of NiAl. Considering these results, it may be concluded that NiAl could be sufficiently corrosion resistant for molten carbonate salt.

3.3. Single cell tests

The above results indicate that Ni and NiAl coatings are efficient for the protection of stainless steel in the anode and wet-seal areas, respectively. In order to verify the

corrosion resistance of Ni and NiAl coatings under cell operation, a corrosion test was performed at 923 K for 10 days in a single cell.

The cross-section of the anode/separator (current-collector) interface area after operation of a single cell for 10 days under 100 mA cm⁻² at 923 K is presented in Fig. 6. The oxide layer formed on the Ni-coated 316L stainless-steel has a thickness of about 3 μm, whereas on the unprotected 316L stainless-steel a very thick (~20 μm) two-layered oxide, which consists of Cr inner and Fe outer layers, is formed.

A NiAl coating (~30 μm) on 316L stainless-steel provided very good protection of substrate 316L stainless-steel during 10 days in a single cell test, whereas 316L stainless-steel was severely corroded, as shown in Fig. 7. The oxide layer formed on the NiAl-coated 316L stainless-steel is Al oxide with a thickness of about 8 μm, whereas the oxide layer (~30 μm) formed on unprotected 316L stainless-steel consists of Cr inner and Fe outer layers.

4. Conclusions

From the present investigation, the following conclusions can be drawn.

(1) A nickel-coating on 316L stainless-steel is very efficient for protecting the material in the anode gas atmosphere of MCFC. By contrast, Ni and Cu exhibit less corrosion resistance than 316L stainless-steel during exposure to the cathode gas atmosphere.

(2) An immersion test of Ni/Al intermetallic compounds reveals that NiAl has superior corrosion resistance.

(3) A NiAl coating (~30 μm) provides very good protection of the 316L stainless-steel substrate during 10 days of single cell testing, whereas untreated 316L stainless-steel is severely corroded.

Acknowledgements

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