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CORROSION BEHAVIOUR OF HIGH TEMPERATURE FUEL CELLS: ISSUES FOR MATERIALS SELECTION

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The corrosion of alloy components in fuel cell is recurring issue and currently it has been leading to low performances of fuel cell and failures. This issue is more prominent in high temperature systems such as molten carbonate and solid oxide fuel cell which operate above 600 °C. The cathode side and anode side corrosion issues have been addressed by many groups but components like current collectors have not. In this framework materials selection is a key issue. Comparing different experiments it can be concluded that the choice of stainless steel (SS) is good choice. In particular, SS316L is good choice but long term test show high degradation of the components. This degradation is mainly due to migration (diffusion) of elements in oxide layer and in base material. Therefore, further studies are needed in order to deeply analyze such behavior. It will allow to better alloy compositions aimed to mitigate degradation and to design alloys showing stable performance of fuel cell.

Key words: stainless steel; high temperature corrosion; fuel cell; molten carbonate fuel cell; diffusion

INTRODUCTION

Fuel cell technology is one of the most promising technologies and currently there is high need for optimization of components involved in fuel cells. A typical fuel cell is based on concept of converting fuel into electricity via electrochemical reaction. Fuel cell converts the hydrogen based fuel to electricity by an electrochemical reaction with oxygen or other oxidizing agents. Fuel cell can produce electricity as long as the fuel is provided this has been one of the major advantages of the system. Today there are many types of fuel cells which operate at different parameters and conditions. In particular, there are five main types of fuel cells, differentiated from one another by their electrolyte. Each type of fuel cell has its advantages and disadvantages.

Polymer electrolyte membrane fuel cell (PEMFC)

A PEM fuel cell uses a solid polymer electrolyte. A PEM fuel cell uses a solid polymer electrolyte. A PEM fuel cell uses a solid polymer electrolyte (Teflon-like membrane), which is an insulator for electrons and good conductor for protons, to exchange the ions between two porous electrodes. These types of fuel cell can operate at temperatures as low as 100 °C.

The advantages of the PEM fuel cell are its high power density and quick start up. Low operating temperatures make the technology competitive in transportation and commercial applications. The major drawback of a PEM fuel cell is its lower operating efficiency which is around 40 – 45 % and use of costly catalyst elements such as platinum. Also, a PEM fuel cell is intolerant to carbon monoxide [1].

Alkaline fuel cell (AFC)

AFC and PEM fuel cells operate at similar temperatures, that is 100 °C, but an AFC fuel cell can reach an efficiency of 60 – 70 %. AFC fuel cells use an aqueous solution of potassium hydroxide (KOH) as an electrolyte, which transports negative charged ions from anode to cathode and releases water as its byproduct. These types of fuel cell have quick startups. A major disadvantage is its high sensitivity to CO_2, this increases the reaction time causing increased consumption of alkaline electrolyte thereby reducing the concentration of hydroxide ions during the reactions. Therefore, it needs a separate system to remove the CO2 from the supply air. The corrosive nature of electrolyte reduces the life span of the fuel cell. Therefore it is not used for commercial applications. These type of fuel cells are used in heavy transportations or large vehicles (i.e. in fleet vehicles and boats in Europe) and space shuttles [1, 2].

Phosphoric acid fuel cell (PAFC)

A phosphoric acid fuel cell (PAFC) operates at about 175 – 200 °C. A PAFC utilizes liquid phosphoric acid as electrodes. Unlike a PEM or AFC, PAFC's are very tolerant to impurities present in reformed hydrocarbon fuels. The chemical reaction involved in these types of

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fuel cells are same as a PEM fuel cell where hydrogen is used as input fuel. Due to its high operating temperature, cogeneration is possible, that is hot water supply as well as generation of electricity depending on the heat and electricity load profile. PAFC and PEM have similar drawback, which is use of expensive elements as catalyst such as platinum [1].

Molten carbonate fuel cell (MCFC)

A molten carbonate fuel cell (MCFC) operates at high temperatures, in the range of 600 – 700 °C. MCFC uses porous electrodes with good conductivity and a carbonate matrix which melt at high temperatures and form molten carbonate electrolyte. MCFC operates on the basis of water-gas shift reaction, where due to its internal reforming utility the carbon-hydrogen based fuel is broken down. A high efficiency of 50 - 60 % and absence of expensive metal catalyst are the major advantages of a MCFC. However, sulfur poising and corrosion of components due to high temperature electrochemical reactions and slow start ups are the major disadvantages. Currently, corrosion of components at high temperatures is a major hurdle, as these types of fuel cells show promise for medium and large power applications, but the corrosion can affect the long term operations and stability of the system. Also, the other costs such as maintenance for large systems might affect the overall cost of the system. Therefore, proper investigation of component corrosion is necessary, as this will prove crucial factor for market deployment of molten carbonate fuel cells [1].

Solid-oxide fuel cell (SOFC)

The SOFC's are similarly high temperature fuel cells, operating at about 1 000 °C. Dense yttria stabilized zirconia, which is a solid ceramic material, is used as its electrolyte. Here oxygen combines with hydrogen to generate water and heat. A SOFC operates at an efficiency of 50 – 60 % and a separate reformer is not required to extract hydrogen from the fuel due to its internal reforming function. Also, waste heat can be recycled to make electricity by a cogeneration system. These advantages make it highly desirable fuel cell. Slow start up, high cost and sulfur poising of the fuel cell are its main drawbacks. Additionally, they are not suitable for larger fluctuations in load demand [1,3]. SOFC's similarly have high temperature corrosion of components too.

The five main types mentioned above and summarized in Table 1 can be classified as parent type fuel cell. Many models present in the market today are derived from these five types. As it can noticed the high temperature fuel cells such as MCFC and SOFC have good efficiency and do not use any precious metal such as a platinum catalyst. Which in turn allows it to be used and deployed in larger quantities. In specific, molten carbonate fuel cells (MCFC) are the most promising cell types. However, one of the major drawbacks of all high temperature fuel cell (MCFC & SOFC) is durability of components, in specific corrosion at high temperatures. The high temperature fuel cells operate well above 600 °C (Table 1) and this causes corrosion at cathode, anode, current collector and separator plates. There have been many investigations with regards to corrosion of cathode and anode, but the current collectors have not been investigated or optimized. The following article will briefly address these topics.

Table 1 **Main fuel cell types [1]**

	PEMFC	PAFC	AFC
Electrolyte	Polymer membrane	Liquid H_3PO_4 (immobilized)	Liquid KOH
Charge carrier	H^+	H^+	OH^-
T / °C	80	200	60 - 220
Catalyst	Pt	Pt	Pt
Cell comp.	C based	C based	C based
Fuel Comp.	H_2, methanol	H_2	H_2

	MCFC	SOFC
Electrolyte	Molten carbonate	Ceramic
Charge carrier	CO_3^{-2}	O^{-2}
T / °C	650	600 - 1 000
Catalyst	Ni	Perovskites
Cell comp.	SS	Ceramic
Fuel Comp.	H_2, CH_4	H_2, CH_4, CO

There have been many iterations of alloys tested for application in fuel cell components. However, apart from specialized components, the materials or alloys used for a fuel cell are not ideal in current generation of fuel cells. Based on cost and performance currently stainless steel 316L is most common material used for components like current collector or separator plates etc. [4]. The SS316L alloy even tough satisfactory, still does not provide a lasting solution as the corrosion at high temperatures is prominent, which leads to failure of system and inefficient operation.

CRITICAL ISSUES BY AREA

A typical MCFC is very suitable fuel cell for energy solution but due the high operating temperatures the cell has some focused areas where corrosion is prevalent and detrimental.

Cathode side

On the cathode side area majority of performance degradation is due to formation of oxide layers due to corrosion of components, which consumes electrolyte material and increases ohmic resistance between electrode and components. Various tests have shown that almost 70 % of electrolyte loss is caused by the cathode-side component's corrosion. This emphasizes the fact that high temperature corrosion of components are one of the major restrictions of high temperature fuel cells or MCFC's. After many iterations modern MCFC's have reduced the initial losses to about 20 % over a time period of 40 000 hours [5].

These electrolyte losses due to formation of oxides in cathode- side area commonly form three distinct layers, two oxide and one metal. For a lithium-potassium-carbonate based electrolyte the outermost layer is an insoluble lithium-ferrous oxide ($LiFeO_2$) formed by a reaction between Fe_2O_3 and Li_2CO_3. $LiFeO_2$ is followed by a compact Cr rich oxide layer and lastly in the chroma depleted region a soluble chromate layer is formed under the oxidizing gas conditions of the cathode side. The chromate layer adds to the losses of electrolyte by preferentially reacting with K_2CO_3 or other alkali carbonate in other electrolytes. Chromate formation also induces voltage loss [6,7]. Thus, reducing the performance of the cell over time. The adoption of austenitic stainless steel is of strategic importance, as due to their high Cr content which yields good high temperature properties and also suitable for long term operations [8-11]. However, various studies show that higher Cr content in 310S steel causes the total electrolyte consumption to be higher when compared to 316L steel [6]. Also, the loss rates are dependent on geometry of components and reducing the contacting surface area can reduce the electrolyte losses. Both the choice of alloy or geometry can reduce the losses but the issues of the corrosion remains in the cathode side components. These are just some major phenomena occurring in the cathode side area. Corrosion can alter the electrolyte distribution within the porous components, which can cause an increase in electrode polarization, matrix ionic resistance and even gas reactants cross over due to matrix drying. Thus it is very crucial to focus on corrosion aspects of the high temperature fuel cells, so that the performance can be increased and lead to a viable energy solution.

Anode Side

Stainless steels do not perform well in the anode-side area (MCFC) as the conditions present are more corrosive than compared to cathode-side. This also leads to formation of multi-layered thick non-protective oxide scales and layers. However, some metals are thermodynamically more stable in such corrosive conditions, such as nickel and copper. Therefore, most of the current applications use nickel clad stainless steel for anode side components. Even though the nickel cladding virtually eliminates growth of oxides and both electrolyte loss and contact resistance. The anode side thermodynamic conditions are highly favorable for carburization reactions since the carbon activity is high (carbon activity, $a_c = 0,1$). Nickel cladding does not obstruct the carbon transport to substrate steel, which would have been not a problem if the substrate steel was not cladded with nickel as oxide layers can stop the carbon transport to the substrate. Nickel at 650 °C has high carbon solubility (0,31 at, %) and diffusivity ($2,68*10^{-10}$ cm^2 s^{-1}). Therefore, leading to the formation of a deep carburization layer below the nickel cladding. This layer consisting of carbides will cause a mechanical failure in future which is an important problem currently [12-14]. Additionally, there are small defects present in the nickel layer irrespective of the method used to deposit, the degree of defect may vary by the method. These defects become a path way to diffusion of elements. Thus, forming small amounts of chroma rich oxide particles at nickel layer grain boundaries. This again compromises the long term performance of MCFC's [4]. The internal oxidation and carburization are the major issues on the anode side. An alloy with high carburization resistance may be able to solve these problems but the studies done in this respect are very few and there is a need to study and understand these alloys and formulate a better alloy for anode side area.

Wet-seal area

The area were the molten carbonate and components come in direct contact and form a leak free gas seal is called as wet seal area. Corrosion is very severe in this area as it may lead to rapid decline of cell performance. Corrosion in this area takes place primarily due to various electro-chemical couples, such as fuel–air, oxidant–air, oxidant–fuel, causing different corrosion rates in different areas of wet-seal. As the cathode side corrosion is different than anode side, as explained above the cathode side experiences an oxide formation and anode side a carburization. Therefore, the components need to be made with respect to the area of contact. Alumina coated alloys with substrate as stainless steel (316L or 310S) are normally used in the wet seal area as it is highly resistant to corrosion. However, under the operating condition of MCFC there is a possibility of aluminum diffusion towards the steel substrate. Thus, compromising the corrosion performance. The effectiveness of the coating also depends on the methods utilized for example, ion vapor deposition, slurry painting, thermal spraying and cladding. Also, a heat treatment of the coated material should be done in order to establish a corrosion resistant layer and high-melting point intermetallic layer. These steps also are very expensive and there is still an issue of aluminum diffusion at 650 °C. [5,6,15] Thus, a study into diffusion behavior at high temperature for different stainless steel alloys is needed.

Current collectors

Current collectors are one of the most crucial components of a fuel cell. This component is subjected to two different hot corrosion environments. Thus, increasing the challenge in selection of a proper alloy. Corrosion heavily impacts an alloy's mechanical properties, electrolyte loss and ohmic resistance, which are very crucial properties for an efficient fuel cell operation. Many high temperature alloys have been evaluated for fuel cell current collectors by various groups (Table 2).

Table 2 **Alloys tested by different groups for MCFC components and their performance**

Alloy	Oxide thickness / mm	Oxide scale resistivity mohm*cm^2	Ref
Mn steel	18	60	[18]
NKK	15	260	[19]
Nitronic-50	25	50	[20]
SS310S	15	260	[20]
SS316L	28	40	[20]
Fe-Cr-Ti	8	370	[12]
Mn Co steel	18	-	[19]
V152	16	150	[19]
Perovskite Coat	12	70	[19]
Co dopped coat	18	-	[10]

The alloys tested consist of all the major know alloy types. The results showed that anode side conditions are more corrosive than cathode side. However, nickel based alloys (e.g. Inconel 600 @ 75 %) with high nickel concentration or pure nickel metals performed well under anodic conditions. These types of alloys are expensive compared to ferritic stainless steels. Also, nickel base high temperature alloys with concentration of nickel less than 50 % perform better than stainless steel, but still not on par for anode-side use. These type of alloys also contain other elements to improve other material properties of the alloy, such as strength. The effects of elements such as molybdenum, tungsten, niobium, titanium, cobalt, manganese etc. are not yet studied in detail under fuel cell corrosive environment. Some studies have shown that they have a detrimental effect on the corrosion performance. Therefore, high nickel alloys are best option currently for use, but a cost versus corrosion resistance comparison shows it's commercially feasible. So, stainless steel such as 310S and 316L have become the current standards to be used as current collector with a coating of nickel on the anode side components. A single –alloy is needed to be developed with good corrosion performance in both conditions in order to eliminate the need to apply a nickel coating [13, 14,16]. This can only be achieved by a proper classification and understanding of the corrosion mechanism in components. There have been many reports of different alloys being applied in MCFC systems to remedy the corrosion issue. The highly oxidative environment of the fuel cells leads to different oxide thickness in different alloys. It is hard to find an alloy which has both low oxide formation and low resistivity. These two aspects are important because the low oxide formation can ensure longer workability and stability of system and low resistivity can increase or maintain the performance. The common trend from the Table 2 that can be inferred is that a ferrous alloys based on chromium, nickel, and manganese are suitable candidates for the fuel cell components such as current collectors etc. However, SS316L the most commonly used alloy in fuel cell parts still does not perform in the most ideal way required. Also, the alloys tested till present are not in the same class as the SS316L. SS316L is Fe-Cr-Ni with trace amount of Mn, Si and Mo, but the other alloys are Fe-Cr-Ni-Mn with trace amounts of Ti and other elements. Even though there are trace amounts it can be seen that the performance variation is high [14, 20].

When alloy components form an oxide layer during the operation, there are additional phenomena which also compromise the operation. Alloys are made of different elements and in such high oxidative environment there are a mix of oxides which form. Also, the oxide layers are not consistent. Ferrous, chromium, manganese etc. oxides which exist together tend to give an uneven and inconsistent layer. This inconsistency can cause many issues. One of the prime examples are migration of the oxide layers causing short circuits. The nickel migration in oxide layers many leads to short circuiting of the entire fuel cell [21]. This migration can attributed to the alloy composition and migration also causes the protective oxide layer, which should be present in order to reduce the corrosion and improve the corrosion resistance, to break and reduce its performance. Figure 1 is an ideal example of such behavior. Figure 1 is an elemental map of the oxide from a test for alloy performance under high temperature and oxidizing environment. Although, the experiment for Figure 1 was not carried out in an ideal fuel cell conditions. The exposure of the alloy was to an environment similar to the conditions of alloys subjected in high temperature fuel cell. It can be seen how two oxide layer over lapping each other and leading to an irregular oxide layer with different element concentration at different points (Figure 1).

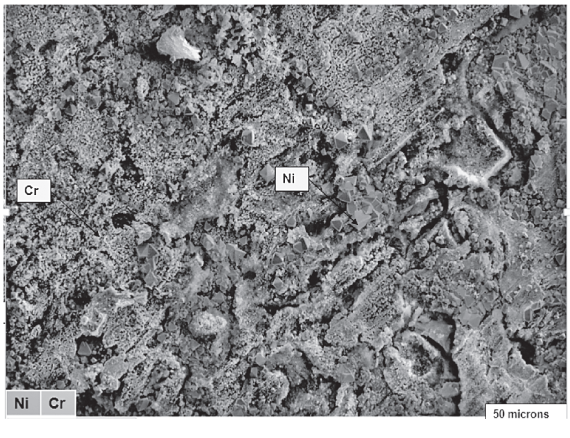

Figure 1. Cr-Ni oxide migration [21]

These kinds of behavior can be seen for ferrous oxides and manganese oxides too. The migration is of a certain elemental oxide is highly depended on the composition of alloy. This is one of the major reasons for an investigation into different alloys and comparison of their performance and mechanisms. Although, there have been tests, few are listed Table 2, with different alloys but they have not been focused on the alloy performance and how compositions effects the operation. This diffusion (migration) of elements is the major degradation occurring in a fuel cell. Current collectors and other key components made from alloys such SS316L can be good solution for short term test but after long term operations the migration or diffusion of elements can pose serious consequences. One such example is forming of an oxide bridge in the cell which causes a short circuit. During the fuel cell operation the nickel coating on the anode side may form spindles and NiO may start to migrate to the other areas [22, 23]. Thus, forming a bridge which will eventually cause short circuit the fuel cell. This is just a small example on how carry on in current collectors can affect the entire operation. As such alloy selection and its corrosion behavior must investigated in detail.

CONCLUSIONS

The corrosion of components is a major issue in all high temperature fuel cells. The corrosion behavior of cathode and anodes has been addressed by many research groups. However, in terms of corrosion of the current collector and its performance, the studies are not adequate. AISI 316 stainless steel has been the best available alloy solution but still the corrosion resistance is not ideal. The migration of elements, formation of oxides and carburization is major cause of degradation and this can be controlled if an ideal alloy composition is found. Up to now few alloys have been tested and there is a need for focused study on alloy performance in fuel cell environment which can help in development of more suitable alloys. The alloy needs to fulfill the corrosion resistance conditions and also should not be expensive. Finally, the high temperature corrosion of alloy components in MCFC can also be useful to other types of fuel cell and in turn reduce loses due to degradation. Therefore, a better understanding is necessary about the nature and behavior of corrosion of different steel alloys. So that a proper alloy can be selected or formulated for usage in fuel cell components. Thus, reducing the corrosion issues and improving the reliability, stability and efficiency of the system. Brining it closer to more practical and usable system for energy needs.

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