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Review

Chromium deposition and poisoning of cathodes of solid oxide fuel cells – A review



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ABSTRACT

Intermediate temperature solid oxide fuel cells (IT-SOFCs) using chromia-forming alloy interconnect requires the development of cathode not only with high electrochemical activity but also with the high resistance or tolerance towards Cr deposition and poisoning. This is due to the fact that, at SOFC operating temperatures, volatile Cr species are generated over the chromia scale, poisoning the cathodes such as (La,Sr)MnO₃ (LSM) and (La,Sr)(Co,Fe)O₃ (LSCF) and causing a rapid degradation of the cell performance. Thus, a fundamental understanding of the interaction between the Fe–Cr alloys and SOFC cathode is essential for the development of high performance and stable SOFCs. The objective of this paper is to critically review the progress and particularly the work done in the last 10 years in this important area. The mechanism and kinetics of the Cr deposition and Cr poisoning process on the cathodes of SOFCs are discussed. Chromium deposition at SOFC cathodes is most likely dominated by the chemical reduction of high valence Cr species, facilitated by the nucleation agents on the electrode and electrolyte surface and/or at the electrode/electrolyte interface, i.e., the nucleation theory. The driving force behind the nucleation theory is the surface segregation and migration of cationic species on the surface of perovskite oxide cathodes. Overwhelming evidences indicate that the surface segregation plays a critical role in the Cr deposition. The prospect of the development in the Cr-tolerant cathodes for SOFCs is presented.

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1. Introduction

The demand for clean, secure and sustainable energy sources has simulated great interests in electrochemical energy storage and conversion technologies such as advanced batteries, fuel cells and supercapacitors. Among them, fuel cell is particularly attractive as fuel cell is considered to be the most efficient, and less polluting power-generating technology.

Fuel cell is an electrochemical device that directly converts the chemical energy of fuels such as hydrogen, natural gas, methanol, ethanol and hydrocarbons to electricity and is a potential and viable candidate to moderate the fast increase in power requirement and to minimize the impact of the increased power consumption on the environment. Among various fuel cells, high temperature solid oxide fuel cells (SOFCs) offer great promise for the most efficient utilization of

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various readily available carbon-containing fuels such as natural gas, hydrocarbons, gasified coal and solid carbon. For stand-alone applications, chemical to electrical efficiency of a SOFC is 45–65%, based on the lower heating value (LHV) of the fuel, which is twice that of an internal combustion engine. SOFCs produce a significant amount of heat, which can be used in combined heat and power (CHP) systems. The overall efficiency of a CHP SOFC system can exceed 70%.

A single cell produces ~ 0.6 – 0.7 V under normal working conditions, therefore in order to obtain desired electric power output, single cells are connected and fabricated together to form a stack using interconnect and sealing materials. The function of interconnect is to connect individual cells electrically in series to form stacks to generate the desired power output with high voltage. Thus, the interconnect materials should have high electrical conductivity, negligible ionic conductivity and should be chemically and structurally stable under both air and fuel environment. There are basically two types of interconnect materials commonly used in SOFCs: doped LaCrO_3 -based ceramic materials and high temperature oxidation resistance metallic materials [1–3].

Significant progress has been made in the decreasing of the operating temperature of SOFCs to 600–800 °C due to the significant reduction of the electrolyte thickness and the development of new electrode materials [4–9]. The significantly reduced operation temperature of SOFCs greatly increases the feasibility of using low cost metallic interconnect materials. Compared to the ceramic interconnect materials, metals have high electronic and thermal conductivity, negligible ionic conductivity, good machinability and low cost. Metallic materials based on the transition metal-based oxidation resistant alloys have been considered to be the primary candidates as the interconnect materials of intermediate temperature SOFCs or IT-SOFCs, due to the economic and easy processing benefits in addition to the high electrical and thermal conductivities. These include Ni(–Fe)–Cr based heat resistant alloys, Cr-based alloys, and chromia-forming ferric stainless steels [10–15]. The alloys with the formation of a protective and semi-conductive chromia scale to minimize further environmental attack during the high temperature operation and with TECs of 11.0 – $12.5 \times 10^{-6} \text{ K}^{-1}$ are the preferred candidates. The conductivity of chromia oxides is $\sim 10^{-2} \text{ S cm}^{-1}$ at 800 °C in air [16]. A good example in this category is Plansee Ducralloy with a composition of 94%Cr, 5%Fe, and 1% Y_2O_3 (as $\text{Cr}_5\text{FeY}_2\text{O}_3$) [17]. To further increase the electrical conductivity of the scale and to reduce the chromium vaporization, a new alloy which contains 0.5% Mn (Crofer22 APU) was developed [18].

Alloys of high temperature oxidation resistance used as interconnect in SOFCs generally contain chromium as an alloying element to form a protective chromium oxide scale (Cr_2O_3). At high temperatures volatile Cr species such as high valent vapor Cr species (e.g., CrO_3 and $\text{Cr}(\text{OH})_2\text{O}_2$) will be generated over the oxide scale layer in oxidizing atmospheres [19,20]. Sources of volatile Cr species can also come from stainless steel components found in the balance-of-plant (BoP) such as heat exchangers [21,22]. Austenitic stainless steel is preferred for high temperature BoP components of a SOFC system due to their better mechanical and corrosion properties. Without effective protective coatings, the gaseous Cr species generated can cause rapid performance

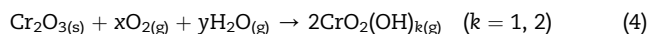
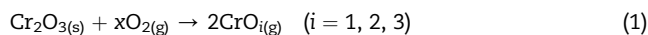
deterioration of SOFC cathodes for the O_2 reduction reaction. Cathode poisoning by chromium from vaporization of the metallic interconnect materials is one of the major degradation mechanisms in SOFCs stacks [23–25].

The interaction between metallic interconnect and cathodes of SOFCs has been extensively investigated in last 10–15 years and great deal of information is available. However, the chromium deposition and poisoning is a complex process because many interrelated factors, such as operating temperature, O_2 partial pressure, air flow, direct or indirect contact with interconnect, applied current load, properties of electrolyte and composition and nature of electrode materials in particular, affect the amount, location and accumulation of chromium deposition. There are significant disagreement and discrepancies on the nature of the deposition and poisoning of volatile Cr species at an air electrode under SOFC operating conditions [26]. This article aims to provide a comprehensive review on the progress and achievement on the clarification and understanding of the chromium deposition and poisoning process and the interrelated factors which affect the interaction between the chromia-forming metallic interconnect and cathodes of SOFCs. The prospect to develop cathode materials with high Cr tolerance is also discussed.

2. Gaseous chromium oxide species: formation, diffusion and determination

2.1. Gaseous chromium oxide species

The basic reason for the Cr volatility is the thermodynamic instability of the chromia scales formed on the chromia-forming alloys at high temperatures, forming gaseous species through the following reactions [20]:



The volatile Cr species from the chromia scale strongly depend on the partial pressure of oxygen and the water content. It has been shown that vapor pressure is much higher in air side than that in the fuel side (the oxygen partial pressure in the SOFC anode side is in the range between 10^{-12} and 10^{-7} Pa) [20]. Thus, the vaporization of Cr species on the SOFC anode could be neglected.

Ebbinghaus et al. studied the equilibrium compositions of fifteen gaseous chromium species over Cr_2O_3 at fixed partial pressures of oxygen (1.0 kPa) and water (10 kPa) in the temperature range from 800 to 1600 K [27]. The thermodynamic calculation predicts that $\text{CrO}_2(\text{OH})_2(\text{g})$ is the dominant vapor species with a small fraction of $\text{CrO}_3(\text{g})$, $\text{CrO}(\text{OH})_3(\text{g})$, $\text{CrO}_2\text{OH}(\text{g})$ and $\text{CrO}(\text{OH})_2(\text{g})$ within the temperature range studied. The

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