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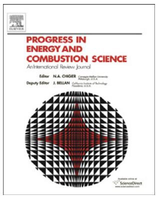

Review

Fundamentals of electro- and thermochemistry in the anode of solid-oxide fuel cells with hydrocarbon and syngas fuels

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ABSTRACT

High fuel flexibility of solid-oxide fuel cells (SOFCs) affords the possibility to use relatively cheap, safe, and readily available hydrocarbon (e.g., CH_4) or coal syngas (i.e., CO-H_2 mixtures) fuels. Utilization of such fuels would greatly lower fuel cost and increase the feasibility of SOFC commercialization, especially for near-term adoption in anticipation of the long-awaited so-called “hydrogen economy”. Current SOFC technology has shown good performance with a wide range of hydrocarbon and syngas fuels, but there are still significant challenges for practical application. In this paper, the basic operating principles, state-of-the-art performance benchmarks, and SOFC-relevant materials are summarized. More in-depth reviews on those topics can be found in Kee and co-workers [Combust Sci and Tech 2008; 180:1207–44 and Proc Combust Inst 2005; 30:2379–404] and McIntosh and Gorte [Chem Rev 2004; 104:4845–65]. The focus of this review is on the fundamentals and development of detailed electro- and thermal (or simply, electrothermal) chemistry within the SOFC anode, including electrochemical oxidation mechanisms for H_2, CO, CH_4, and carbon, as well as the effects of carbon deposition and sulfur poisoning. The interdependence of heterogeneous chemistry, charge-transfer processes, and transport are discussed in the context of SOFC membrane-electrode assembly modeling.

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1. Introduction

Solid-oxide fuel cells (SOFCs) are the most efficient devices known to convert the chemical energy of a fuel directly into electricity [1]. Research on SOFCs is vast, and their development has been long and continuous, primarily because these devices carry a set of attractive features [1–17]. SOFCs (and other fuel cells) offer high conversion efficiencies and an environmentally friendly alternative to modern combustion-based systems, but their oxygen-ion-conducting electrolyte and high operating temperature (600–1000 °C) allows greater fuel flexibility than most other fuel cells (though materials selection and sealing can be an issue at very high temperatures).

The high fuel flexibility of SOFCs affords the possibility to use relatively cheap, safe, and readily available carbon-based fuels instead of hydrogen. Additionally, CO_2 capture in SOFC-based systems can be achieved at lower cost and lower system complexity than in conventional combustion systems [18,19], because the fuel and oxidizer in an SOFC are not in direct contact as in traditional combustion processes. This facilitates CO_2 sequestration without the need for expensive gas-separation technologies.

Despite the apparent promise and advantages of SOFC as an energy-conversion technology, several obstacles must be overcome before SOFCs move beyond the early stages of commercialization. For example, improving efficiencies, finding catalysts with higher tolerances to fuel impurities, preventing deactivation of the anode as a result of carbon deposition when using carbon-based fuels, long-term operational reliability and durability, sealing problems, stack and system integration issues, and overall production costs.

A comprehensive review of the operating principles, performance, and current challenges associated with SOFCs utilizing hydrocarbon and syngas fuels can be found in Kee and co-workers [6,7] and McIntosh and Gorte [20]. In this paper, we provide a further review of the research and developmental status of typical hydrocarbon- or coal-syngas-fueled SOFCs by focusing on the following topics:

- fundamental mechanisms of electrode chemical and electrochemical reactions, specifically in the anode;
- anode materials, particularly in the context of carbon deposition and tolerance to sulfur poisoning;
- coupling of electro- and thermochemistry with transport in physics-based models of SOFC membrane-electrode assemblies.

A better understanding of these topics is essential for further improvement and optimization of SOFCs operating on hydrocarbon or coal-derived fuels.

2. Operating principles and materials

The electrochemical charge-transfer reactions and some of the thermochemical (reforming) reactions in an SOFC take place in the membrane-electrode assembly (MEA)[1] as shown in Fig. 1. At the positive electrode (cathode), oxygen is reduced to generate oxygen ions O^{2-}, which are conducted through the electrolyte to the negative electrode (anode), where they electrochemically oxidize the fuel (e.g., CO, H_2, CH_4) to produce electrons, which flow through the external electrical circuit generating a current. During this process, the Gibbs free energy (or chemical potential energy) of the global reaction of fuel and oxidizer is converted into electricity and heat.

2.1. Requirements of the membrane-electrode assembly

The membrane-electrode assembly is the heart of any fuel cell. In an SOFC, the MEA consists of a dense oxygen-ion-conducting electrolyte sandwiched between two porous electrodes. On the anode side, gas species in the fuel channel are transported through the porous cermet network of the electrode to electrochemically

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[1] Several different terms are used in the literature to describe the single-cell unit of a fuel cell stack, more often than not being associated with a specific type of fuel cell. We prefer to use membrane-electrode assembly, but tri-layer or positive-electrode electrolyte negative-electrode (PEN) also appear in the SOFC literature.