

Electrochemical oxidation of methanol and ethanol on Cu/CeO₂, Cu-Co/CeO₂ and LSV anodes for Solid Oxide Fuel Cells

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Introduction

Fuel cells are electrochemical devices that can produce electric power at very high efficiencies directly from the oxidation of hydrogen. Among the various types, solid oxide fuel cells (SOFC) are now receiving considerable attention because of their ability to operate also with other fuels, such as carbon monoxide and methane. Researchers are focusing specifically on the direct oxidation of traditional fuels [1] and of fuels derived from renewable sources [2]. Significantly, there are already examples of commercialization of direct hydrocarbon SOFC [3]. For this purpose the traditional Ni-YSZ (cermet of nickel and yttria-stabilized zirconia) anodes suffer deactivation due to coke formation, and hence, the focus is on the development of alternative anodes.

In this study we present the results of a study on the direct oxidation of methanol and ethanol on Cu/CeO₂, Cu-Co/CeO₂ and LSV (La_{0.7}Sr_{0.3}VO_{3-δ}) anodes at temperatures ranging from 700 to 800°C.

Materials and Methods

Metal/ceria anodes were prepared on electrolyte-supported cells by multi-step impregnation with metal-nitrate precursors on a porous YSZ layer. LSV perovskite powders were prepared by the citric-acid process and heat-treated at 900°C in a reductive atmosphere. LSV anodes were obtained by spray-painting a slurry of the perovskite powder, YSZ and isopropanol on the electrolyte pellet and then sintering at 1200°C in 9 % H₂/He gas mixture for 4 hr. Pt paste was used for the cathode and reference electrode.

These cells were tested in H₂ (dry and humidified), CO, H₂/CO mixtures, methanol and ethanol. The outlet gas composition was monitored by gas chromatography and mass-spectrometry. Performance and short-term stability were determined by measuring the current vs. voltage response of the cell and by galvanostatic steps, respectively. The anodic activation overpotential was obtained by cyclic-voltammetry (CV) and impedance spectroscopy (EIS) using a reference electrode (i.e. three-electrode configuration). CV and EIS results, obtained at different temperatures and partial pressures of H₂ and CO, were analyzed similarly to Primdahl et al. [4] and Boukamp [5].

Results and Discussion

Cu/CeO₂ and Cu-Co/CeO₂ anodes showed similar electro-catalytic activity and did not suffer deactivation caused by coking when fuelled directly with alcohols. Interestingly, metal/ceria anodes exhibited higher activity in ethanol than in H₂/CO mixtures - equivalent to ethanol in C/H content - at large applied potentials above + 0.3 V vs OCP (see Figure 1).. This effect was probably caused by the oxidation of an intermediate species of the ethanol

decomposition and is likely related to the low fuel-utilization and residence time used. The apparent performance (i.e. not normalized per unit active area) of LSV anode was inferior to metal-ceria anodes. Furthermore, LSV perovskites were unstable to redox cycling, leading to the irreversible formation of La_{0.7}Sr_{0.3}VO₄, which is a poor electronic conductor. These anodes, however, were resistant to carbon formation.

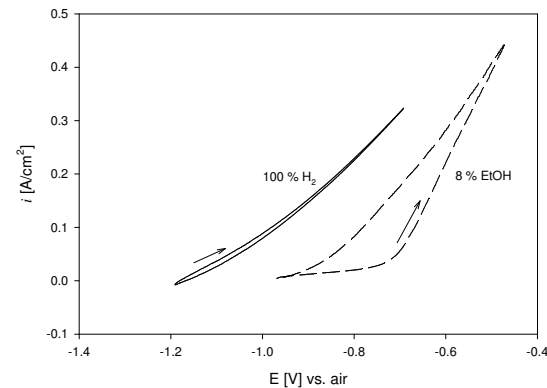


Figure 1. Cyclic voltammetry of Cu-CeO₂ anodes in H₂ and ethanol (EtOH) at 800 °C.

Significance

Development of SOFC operating with traditional and renewable fuels is significant in the context of efficient energy production and reduction of carbon dioxide emissions. Few studies have been published on SOFC operating directly on alcohols. In this work, alternative SOFC anodes have been tested with methanol and ethanol to determine their activity and stability, and expand the research in this developing area.

References

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