



Reactions and mass transport in high temperature co-electrolysis of steam/CO₂ mixtures for syngas production



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HIGHLIGHTS

- Steam is the primary reactant in co-electrolysis of steam/CO₂ mixtures.
- CO₂ contributes to the electrochemical performance near limiting currents.
- CO₂ reduction is predominantly governed by thermochemical reactions.
- Chemical kinetics and mass transport play a significant role in co-electrolysis.
- Syngas yield and selectivity are largely dependent on operating conditions.

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ABSTRACT

High temperature co-electrolysis of steam/CO₂ mixtures using solid oxide cells has been proposed as a promising technology to mitigate climate change and power fluctuation of renewable energy. To make it viable, it is essential to control the complex reacting environment in their fuel electrode. In this study, dominant reaction pathway and species transport taking place in the fuel electrode and their effect on the cell performance are elucidated. Results show that steam is a primary reactant in electrolysis, and CO₂ contributes to the electrochemical performance subsequently in addition to the effect of steam. CO₂ reduction is predominantly governed by thermochemical reactions, whose influence to the electrochemical performance is evident near limiting currents. Chemical kinetics and mass transport play a significant role in co-electrolysis, given that the reduction reactions and diffusion of steam/CO₂ mixtures are slow. The characteristic time scales determined by the kinetics, diffusion and materials dictate the cell performance and product compositions. The fuel electrode design should account for microstructure and catalysts for steam electrolysis and thermochemical CO₂ reduction in order to optimize syngas production and store electrical energy effectively and efficiently. Syngas yield and selectivity are discussed, showing that they are substantially influenced by operating conditions, fuel electrode materials and its microstructure.

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1. Introduction

Production of synthetic hydrocarbon fuels from co-electrolysis of steam/CO₂ mixtures using renewable energy has been introduced as a promising solution to mitigate both global climate

change and power fluctuation. As climate change continues, intensive research has been conducted to lower the emissions of green-house gases, in particular, carbon dioxide [1]. To address this environmental issue, capturing carbon dioxide has been extensively investigated, which in turn leads to the needs for the development of its conversion technology [2]. Co-electrolysis has been proposed to convert carbon dioxide and steam into the syngas composed of carbon monoxide and hydrogen, which can be processed further to produce higher hydrocarbon fuels [3,4]. Steam

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and CO₂ could be electrolysed separately and mixed to produce syngas, but electrolysing them simultaneously benefits from a higher energy efficiency and prevention of harmful problems such as carbon deposition [5]. In addition, as renewable energy technologies have been implemented in the market, it is necessary to develop methodologies to alleviate their power fluctuation and match supply and demand. This requires the development of large-scale energy storage that is cost-effective, energy-efficient and ready to be deployed at widespread regions [6]. In this regard, co-electrolysis is one of the best technologies that store electrical energy in the form of chemical energy whose energy density is higher than any other forms of energy and which can be readily used for power production. Co-electrolysis can be implemented with a variety of renewable electrical sources and has economic competitiveness [3,7,8]. Therefore, co-electrolysis of steam/CO₂ mixtures can contribute simultaneously to CO₂ reduction and energy storage.

Solid oxide cells (SOC) have been shown to exhibit excellent capabilities for CO₂ reduction and energy storage through high-temperature co-electrolysis of steam/CO₂ mixtures utilizing renewable energy sources. These cells have been demonstrated for power production from hydrocarbon fuels when operating as solid oxide fuel cells (SOFC) [9]. Recently, they have also shown considerable potentials as solid oxide electrolysis cells (SOEC) that can convert steam/CO₂ mixtures to the syngas by applying external electrical currents at high temperature above 800 °C [10]. In comparison with low-temperature co-electrolysis, they take advantage of faster steam/CO₂ dissociation kinetics given that reactions occurring in the fuel electrode are increasingly endothermic with raising temperature [4]. Moreover, since materials used for SOEC are the same as those of SOFC and have been extensively examined through SOFC research, investigation on the feasibility and durability of SOEC for co-electrolysis proceeds relatively fast. To make this technology viable, it is essential to maximize the syngas production rate and products selectivity by controlling fuel electrode reactions, CO₂/H₂O reduction, and mass transport. The fact that the ultimate goal of high-temperature co-electrolysis is syngas production makes the examination of the fuel electrode reacting environment significantly important [11]. However, given the complex thermo-electrochemical reactions and mass transport taking place in the fuel electrode of SOEC, they have not been elucidated in detail.

Experimental studies conducted so far have used sparse operating conditions varied in an unsystematic manner, which cannot elucidate the complex reactions and species transport. Risø National Laboratory for Sustainable Energy characterized polarization of co-electrolysis using their planar cells [10,12,13]. Considering a small number of sets of gas compositions, they examined the area specific resistance and electrochemical impedance spectra. It was discussed that both CO₂ and steam are electrochemically reduced, and reverse water gas shift (RWGS) reaction also plays a role during co-electrolysis. However, the sets of gas compositions they used were varied unsystematically, and no quantitative gas products analysis was reported, weakening their investigation on the thermo-chemical reactions and species transport in the fuel electrode and their effect on the cell performance. Idaho National Laboratory tested their 10-cell planar stack at a number of operating conditions including gas inlet compositions, flow rates and temperatures [5,14]. Although they measured gas products quantitatively, the range of variation in their operating conditions was limited, which makes it difficult to correlate the quantitative analysis with characterization of the fuel electrode reactions and mass transport. Dominant reaction pathways and the role of each reactant have not been elucidated, and the effect of chemical reactions and mass transport on the cell performance has not been discussed.

Moreover, syngas yield and its selectivity have not been defined or examined, which is key for syngas production.

In this study, thermo-electrochemical reactions and mass transport taking place in the fuel electrode of high-temperature SOC for co-electrolysis and their effect on the cell performance are experimentally examined. An experimental setup was designed for the co-electrolysis of steam/CO₂ mixtures, enabling not only electrochemical characterization but also quantitative analysis of reaction products. Key operating parameters including a steam concentration, a molar ratio of CO₂ to steam, temperature and flow rate, all of which influence the kinetics and species transport, were varied systematically. Focusing on the fuel electrode phenomena, the importance of chemical kinetics and species transport in determining a primary reactant, the effect of CO₂ on the cell performance, syngas production rate and its selectivity is investigated. In addition, dominant reduction pathway of steam/CO₂ mixtures is elucidated, differentiating thermo- and electro-chemical reactions. The syngas yield and its selectivity were defined and characterized quantitatively by reaction products analysis for the first time. The dependence of the cell performance encompassing polarization, syngas yield and its selectivity on fuel electrode materials, its microstructure and operating conditions is also discussed.

2. Experimental

The fuel electrode-supported cells used in this study consist of a Ni-YSZ support, Ni-YSZ fuel electrode functional layers, YSZ electrolyte, a GDC interlayer, LSC-GDC air electrode functional layers and LSC air electrode current collecting layers. For fabrication of the support, NiO-YSZ composite powders (NiO, Sumitomo Metal Mining, Japan and 8YSZ (8 mol% Y₂O₃ stabilized ZrO₂, TZ-8Y), Tosoh Corp., Japan) were spray-dried to produce the granule which was then compacted by uni-axial pressing. To increase the porosity within the support, 30% (volume basis) PMMA was added to the granule. The fuel electrode functional layers were screen-printed on the support using NiO-YSZ cermet paste prepared by mixing the NiO-YSZ composite powders with solvent (α -terpineol, Kanto chemical, Japan), plasticizer (dibutyl phthalate, Junsei chemical, Japan), dispersant (Hypermer™ KD-6, Croda, United Kingdom) and binder (ethyl cellulose, Sigma–Aldrich, USA). The YSZ electrolyte layers were subsequently screen-printed, and co-fired at 1380 °C. The GDC paste was prepared by mixing precursor powders (Rhodia, France) with the solvent, plasticizer, dispersant and binder. The GDC interlayer was applied on top of the electrolyte by screen printing and sintered at 1250 °C. Cell fabrication was completed by screen printing LSC-GDC air electrode functional layers (LSC precursor powders from Kceracell, Korea) and LSC air electrode current collecting layers, followed by the sintering process at 950 °C. Fig. 1(a) shows the 2 cm × 2 cm and 5 cm × 5 cm cells used in this study for co-electrolysis of steam/CO₂ mixtures. To obtain gas-tight sealing, gasket-type composite sealants containing binary ceramic fillers within the glass matrix [15] for high-temperature operation (~800 °C) were employed between the electrolyte face on the air electrode side of the cell and a metallic end-plate. These sealants were designed to match their thermal expansion coefficient with that of the metallic end-plates and to reduce the thermal stress between them. The sealants were fabricated using 65% (volume basis) Pyrex glass (Iwaki, Japan), 10% (volume basis) alumina particulate (ALM-43, Smitomo Chem., Japan) and 25% (volume basis) alumina platelet (Nano Fluid, Korea).

Electrochemical characterization and reaction-products analysis were performed by using a co-electrolysis cell testing system developed in this study, as illustrated in Fig. 1(b). The Inconel-based

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