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Short communication

High-temperature electrolysis of CO_2–enriched mixtures by using fuel-electrode supported $La_{0.6}Sr_{0.4}CoO_3$/YSZ/Ni-YSZ solid oxide cells

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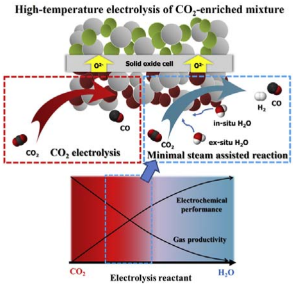
HIGHLIGHTS

- *In-situ* steam supply to dry CO_2-enriched mixtures lowers electrochemical resistance.
- Such operation mechanism is effective at low electrolysis current density.
- A small amount of external steam supply may expand the operating current regime.
- External steam supply degrades gas productivity (CO_2 conversion and CO selectivity).
- Low power demand and high gas productivity can be achieved by optimal steam supply.

GRAPHICAL ABSTRACT



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ABSTRACT

To mitigate CO_2 emissions, its reduction by high-temperature electrolysis using solid oxide cells is extensively investigated, for which excessive steam supply is assumed. However, such condition may degrade its feasibility due to massive energy required for generating hot steam, implying the needs for lowering steam demand. In this study, high-temperature electrolysis of CO_2-*enriched* mixtures by using fuel-electrode supported $La_{0.6}Sr_{0.4}CoO_3$/YSZ/Ni-YSZ solid oxide cells is considered to satisfy such needs. The effect of internal and external steam supply on its electrochemical performance and gas productivity is elucidated. It is shown that the steam produced *in-situ* inside the fuel-electrode by a reverse water gas shift reaction may decrease significantly the electrochemical resistance of dry CO_2-fed operations, attributed to self-sustaining positive thermo-electrochemical reaction loop. This mechanism is conspicuous at low current density, whereas it is no longer effective at high current density in which total reactant concentrations for electrolysis is critical. To overcome such limitations, a small amount of external steam supply to the CO_2-*enriched* feed stream may be needed, but this lowers the CO_2 conversion and CO/H_2 selectivity. Based on these results, it is discussed that there can be minimum steam supply sufficient for guaranteeing both low electrochemical resistance and high gas productivity.

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1. Introduction

Global agreement on climate change has stimulated extensive research and development of mitigation technologies for CO_2 emissions. As compared to other anthropogenic greenhouse gases (e.g., CH_4 and N_2O), the amount of its emissions is tremendous, given that the current infrastructure is based on carbon intensive economies which produce massive CO_2 [1]. To alleviate its emissions and catastrophic environmental impacts, a number of promising technologies enabling its sequestration or conversion have been investigated [2,3]. Especially, converting it to other forms of value-added products has been shown to exhibit great potentials in the perspective of economics and sustainability [4,5]. To provide such functionality, utilizing the surplus power from renewable energy sources to electrolyze CO_2 has been considered as one of the most effective methods, for which high-temperature solid oxide cells are used [3–8]. If such process produces hydrogen along with carbon monoxide, the syngas can be provided to post-processing systems to synthesize higher hydrocarbon fuels or chemicals [3]. In this regard, wet CO_2 electrolysis using high-temperature solid oxide cells has been intensively examined to mitigate its emissions and produce the syngas [4,5].

To demonstrate the feasibility of high-temperature CO_2 electrolysis, previous studies have assumed excessive steam supply to the fuel-electrode. Dry CO_2 electrolysis may result in substantial carbon deposition on the Ni surface embedded in the fuel-electrode, which deteriorates electrochemical performance and CO_2 conversion efficiency [9–11]. The carbon deposition can be avoided by supplying steam to the fuel-electrode. Moreover, as stated above, syngas can be formed if wet CO_2 electrolysis is assumed, in which high hydrogen throughputs have been typically targeted [12,13]. To meet these needs, excessive steam is supplied to the CO_2 feed stream, making the volumetric ratio of steam to CO_2 larger than the unity. However, in practical applications, high-temperature steam sources may not be available, and massive energy is needed to generate a high flow rate of hot steam. This definitely degrades the thermodynamic efficiency and cost-competitiveness of high-temperature CO_2 electrolysis. Furthermore, to synthesize value-added products with high carbon contents, the reduction of CO_2 needs to be prioritized against hydrogen production. Note that the primary goal of CO_2 electrolysis using high-temperature solid oxide cells is to convert the greenhouse gas mitigating its emissions. All these require CO_2 electrolysis to proceed with lower steam supply. In this reason, high-temperature electrolysis of CO_2-enriched mixtures should be investigated, which has been ignored in the previous studies.

The effect of steam supply to the CO_2-enriched mixtures on electrochemical performance and gas productivity needs to be elucidated in a systematic way. The reacting environment in the fuel-electrode of solid oxide cells is quite complex, given that thermochemical reactions are accompanied with electrochemical reactions [14]. Reactants and products are intertwined by simultaneous electrolysis and reverse water gas shift reactions. This also makes internal steam supply possible even if no steam content is present in the original feed stream. Given this complexity, it is necessary to isolate and characterize the effect of internal and external steam supply to the CO_2-enriched mixtures by controlling systematically the feed gas compositions. In this study, to meet such needs, both dry and wet CO_2–enriched feed streams to solid oxide cells supported by a Ni-cermet fuel-electrode were considered while maintaining the total feed gas flow rate and gas concentrations constant. By controlling the extent of internal and external steam supply, its effect on electrochemical performance and gas productivity was discussed in detail, which may envision possibilities for optimal steam supply guaranteeing both low power demand and high gas productivity.

2. Experimental

Solid oxide cells used in this study are based on the planar-type structure supported by Ni-yttria-stabilized zirconia (YSZ) substrates. Multiscale layers are successively placed on top of the substrate, which include Ni-YSZ fuel-electrode functional layers, YSZ electrolyte, gadolinium-doped ceria (GDC) interdiffusion barrier layer, lanthanum-strontium-cobalt (LSC)-GDC air-electrode functional layers and LSC air-electrode current collection layers. The raw precursor powders for such layers were obtained from NiO (Sumitomo Metal Mining, Japan), YSZ (8 mol% Y_2O_3 stabilized ZrO_2 (TZ-8Y), Tosoh Corp., Japan), GDC (gadolinium-doped ceria, Rhodia, France), and LSC ($La_{0.6}Sr_{0.4}CoO_3$, Kceracell, Korea). For fabrication of the fuel-electrode substrate (1 mm thick), NiO, YSZ and a poly(methyl methacrylate) pore-forming agent were mixed with dispersant (HypermerTM KD-6, Croda, United Kingdom), binder (ethyl cellulose, Sigma-Aldrich, USA) and plasticizer (dibutyl phthalate, Junsei chemical, Japan) in ethanol and ball-milled for 24 h. NiO-YSZ composite granules were synthesized by a spray drying method, which were subsequently compacted uni-axially at a pressure of 60 MPa. The substrate was annealed to secure the mechanical strength and to stack the electrodes and electrolyte on it. The pastes for the fuel-electrode functional layers, electrolyte, interdiffusion barrier layer, air-electrode functional layers, and air-electrode current collecting layers were prepared by mixing corresponding powders with the dispersant, binder and plasticizer in solvent (α-terpineol, Kanto chemical, Japan) and using a planetary mill. The fuel-electrode functional layers (8 μm thick) and electrolyte (10 μm thick) were screen-printed on the substrate and co-sintered at 1400 °C. The interdiffusion barrier layer (4 μm thick) was screen-printed on top of the YSZ electrolyte and sintered at 1250 °C. Subsequently, the air-electrode functional layers (8 μm thick) and air-electrode current colleting layers (14 μm thick) were screen-printed and sintered at 950 °C. The microstructural characteristics of the prepared cell can be found in Supplementary Fig. S1 and Table S1. Note that the fuel-electrode substrate and functional layers have similar particle sizes of ~1 μm, but they have different pore sizes and porosities such as ~5 μm and 0.38 for the former and ~700 nm and 0.2 for the latter. The size of the unit cells is 2 cm × 2 cm, and the effective electrode area is 1 cm × 1 cm. Further details of cell preparation can be found in Refs. [15,16].

The effect of internal and external steam supply on high-temperature electrolysis of CO_2-enriched mixtures was investigated by using a solid oxide electrolysis cell testing system which is detailed in Ref. [16]. In the fuel-electrode, the total feed gas flow rate of 100 sccm and supplied reactive gas concentrations of 70% were maintained constant throughout the study. In the air-electrode, air with the flow rate of 200 sccm was used. The constant cell temperature of 800 °C was assumed. The steam concentration in the fuel flow was controlled by a humidifier equipped with the reverse osmosis system (RO-Pure Plus, Premier, USA). Electrochemical characterization was performed by a frequency response analyzer and potentiostat (Solartron 1260/1287, Solartron Analytical, United Kingdom). Quantitative reaction-products analysis was conducted by an online mass spectrometer (Hiden HPR-20 QIC, USA) and gas chromatography (Agilent 7890B, USA), both of which are connected to the tail-end of the cell-testing system.

3. Results and discussion

In the course of CO_2 reduction by high-temperature electrolysis, low power demand and high gas productivity should be obtained for viable operations. The former is directly related to the internal electrochemical resistance of solid oxide cells, and the latter is determined by a CO_2 conversion rate and products selectivity. All these are influenced substantially by reactant compositions in the fuel-electrode of solid oxide cells, in particular, the steam concentration and its molar ratio against CO_2 [16]. The steam can be either produced *in-situ* by the reverse water gas shift (RWGS) reaction or supplied externally in the CO_2-enriched feed stream. In this sense, the two sets of feed gas compositions (namely, internal and external steam supply) were examined in this study, as summarized in Table 1. Given that reactants pass through