High-temperature electrolysis of simulated flue gas in solid oxide electrolysis cells

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ABSTRACT

The feasibility of the solid oxide electrolysis cell (SOEC) electrolysis of flue gas based on an electrolyte-supported LSCM-GDC/SSZ/LSCF-GDC (LSCM: $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$) single cell is comprehensively evaluated. Current density-voltage curves (I-V) and electrochemical impedance spectroscopy data (EIS) are recorded to characterize the electrochemical performance of SOEC. The results confirmed that the LSCM-GDC fuel electrode is chemically stable in the flue gas atmosphere. The results also showed that simulated SO_2 with concentration of 15 ppm in the flue gas has a negligible influence on the cell at an electrolysis current density of ~0.2 $A\,cm^{-2}$. The O_2 in the flue gas increases the electrolysis activity in the fuel electrode, thereby improving the efficiency of the SOEC electrolysis of flue gas. The co-existence of SO_2 and O_2 in flue gas can increase the electrolysis activity of SOEC electrolysis. The total resistance of the SOEC single cell at 800 °C under OCV is 2.21 $\Omega\,cm^2$, indicating that the SSZ-electrolyte-supported SOEC can be practically used for the effective SOEC electrolysis of flue gas containing SO_2 and O_2. The cell showed a stable voltage of 1.201 V for more than 100 h for the electrolysis of flue gas with SO_2 and O_2 at a current density of 0.5 $A\,cm^{-2}$ and at a temperature of 800 °C. The post-mortem analysis showed that the microstructures of all cell components are stable after the SOEC long-term durability test.

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1. Introduction

The increasing consumption of carbon-based fossil fuels in recent years has greatly increased the amount of greenhouse gas emissions (typically CO_2) in the atmosphere, leading to global warming and intense environmental degradation [1,2]. Therefore, the development of carbon-free/neutral energy technologies and environment-friendly alternatives to fossil fuels must be explored to mitigate the issues [3,4]. Solid oxide electrolysis cell (SOEC) is an environmentally friendly energy conversion device that can convert electrical energy into chemical energy efficiently [5–11]. SOEC can convert the renewable energy or the excess electricity produced from a power plant into H_2 or syngas ($CO + H_2$) using H_2O or H_2O and CO_2. Moreover, operating SOEC at high temperature can reduce the electrical energy requirements of the electrolysis process, improve the electrode kinetics, and reduce the SOEC electrolyte resistance, hence reducing the losses in SOEC. If the waste heat from power stations or other high-temperature industrial processes is applied, then SOECs can generate H_2 or syngas at a significantly higher efficiency demonstrating the heat pump-like advantages [12,13]. The syngas itself is a chemical energy storage, but it can also be used as the feedstock for the production of synthetic hydrocarbon fuels via the Fischer–Tropsch process [14]. Therefore, using SOECs to recycle CO_2 from energy systems presents an attractive solution to both CO_2 storage and greenhouse effect [15].

When using SOECs in the high-temperature co-electrolysis of CO_2 and H_2O, both CO_2 and H_2O are fed as reactants into the fuel electrode side of the cell, while oxygen ions are transported to the oxygen electrode through the electrolyte. Oxygen is evolved at the

oxygen electrode side, while syngas is produced at the hydrogen electrode side [2]. An SOEC can undergo a reverse process exhibiting a high-temperature solid oxide fuel cell (SOFC). Thus, SOEC technology can be built based on the rich experience of SOFC technology [16,17]. Achieving a highly stable electrolysis performance is one of the main challenges in the co-electrolysis of CO_2 and H_2O. Currently, most researches related to SOEC are on modelling and material studies. In the modelling studies of SOEC, Narasimhaiah et al. [18] developed a modified Butler—Volmer model for the simulation of CO_2 reduction by considering multistep single-electron transfer reactions. Ni [19,20] presented electrochemical model, 1D model and 2D thermal model of SOEC to study the co-electrolysis of CO_2 and H_2O by considering its heat/mass transfer and chemical/electrochemical reactions. Data-driven model based on extreme learning machine algorithm was also developed to model the performance of SOEC under co-electrolysis processes in our previous study [7]. For the material studies, Yttrium-stabilized zirconia (YSZ) is the most commonly used electrolyte for co-electrolysis. However, YSZ does not have a sufficiently high ionic conductivity to be utilized at lower operating temperatures. ZrO_2 doped with Sc_2O_3 (SSZ) electrolyte has a higher oxygen ionic conductivity than YSZ and has been used in SOFC [21]. However, when developing SOEC oxygen electrodes, the traditional LSM/YSZ material degrades due to the delamination of the oxygen electrode and the formation of pores at the YSZ grain boundary [22—24]. $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) can be widely used to suppress this delamination problem [25]. The Ni-YSZ composite is the most commonly used fuel electrode material in SOEC [24,26]. However, using Ni as a fuel electrode requires a strongly reducing atmosphere such as H_2 or CO to avoid the oxidation of Ni into NiO especially at OCV conditions, which in turn leads to the loss of electronic conductivity and the failure of the fuel electrode [27]. $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) has a perovskite structure and is a redox-stable electrode material with excellent electrocatalytic properties [28]. LSCM has also been identified as one of the most promising materials for replacing Ni-based cermets in SOFC [29,30]. The LSCM electrode is stable in both extreme oxidizing and reducing atmospheres [27,31].

Flue gas or stack gas is an exhaust gas generated through the combustion processes of fossil fuels. Apart from CO_2, flue gas components also contain other air pollutants that must be eliminated or minimized via special cleaning procedures before releasing the gas to the atmosphere [32,33]. Flue gas is usually composed of CO_2, water vapor, nitrogen, and excess oxygen from the intake combustion air. This type of gas may also contain a small percentage of air pollutants, such as NO_x, SO_x and CO [33—35]. The composition of this gas depends on the type of fuel and the combustion conditions (e.g., the air-fuel ratio). Given its large amount of CO_2 and H_2O, directly reusing flue gas to generate syngas via SOEC electrolysis (rather than CO_2 and H_2O co-electrolysis) will greatly increase the availability of this resource around these regions. Moreover, direct flue gas electrolysis would eliminate the tedious and energy-intensive CO_2 capture. Nevertheless, the high-temperature electrolysis of flue gas using SOECs needs to be explored further.

Accordingly, this work aims to evaluate comprehensively the feasibility of the SOEC electrolysis of flue gas, especially when containing SO_2 and O_2. The simulated flue gas was composed of CO_2, H_2O, SO_2, O_2, and balance gas N_2 (N_2 can be omitted when using flue gas from oxy-combustion plant). The electrochemical performance and stability based on electrolyte-supported SOEC with a configuration of LSCM-GDC/SSZ/LSCF-GDC (GDC: $Gd_{0.1}Ce_{0.9}O_{1.95}$) were characterized and compared under different operating conditions. The finding of this work may provide a valuable reference for the SOEC electrolysis of flue gas in practical applications.

2. Experimental

SSZ $((Sc_2O_3)_{0.10}(CeO_2)_{0.01}(ZrO_2)_{0.89}$, $D_{50} = 0.5{-}0.7 \, \mu m)$, GDC $(D_{50} = 0.1{-}0.4 \, \mu m)$, and LSCF $((La_{0.60}Sr_{0.40})_{0.95}Co_{0.20}Fe_{0.80}O_{3-x}$, $D_{50} = 0.7{-}1.1 \, \mu m)$ powders were purchased from Fuel Cell Materials, US. The perovskite LSCM powders were synthesized by using a conventional solid-state reaction method. Stoichiometric amounts of La_2O_3 (99.9%), $SrCO_3$ (99.9%), Cr_2O_3 (99.9%), and $MnCO_3$ (99.9%) were mixed in ethanol and milled for 8 h. After drying and grinding, the powders were calcined at 1200 °C for 12 h.

SSZ-supported button cells were prepared by using the tape-casting method and were sintered at 1500 °C to obtain dense electrolyte substrates. The preparation of the slurry and the tape-casting process of SSZ supports were described in detail in our previous study [36]. The obtained SSZ electrolyte had a diameter of 20 mm and a thickness of 200 μm. A 50—50 wt % of LSCM and GDC powders was mixed with a proper amount of polyethylene glycol to form the fuel electrode slurry. The mixture was applied on one side of the SSZ electrolyte by using the screen printing technique and was subsequently sintered at 1250 °C for 2 h to form a porous LSCM—GDC composite fuel electrode. Similarly, a 50—50 wt % of LSCF and GDC powders was mixed with a proper amount of polyethylene glycol to form the oxygen electrode slurry. The mixture was applied on the other side of the SSZ electrolyte by using the screen printing technique and was subsequently sintered at 900 °C for 2 h to form a porous LSCF—GDC composite oxygen electrode. A porous Pt layer was coated on both electrodes with an effective active area of 0.5 cm^2 to serve as the current collectors, and these electrodes were then sintered at 800 °C for 30 min. The thicknesses of the LSCM—GDC fuel electrode and the LSCF—GDC oxygen electrode were approximately 35 μm.

Fig. 1 shows the experimental setup for the SOEC electrolysis of flue gas. The cell was fixed and sealed in an aluminum tube via a glass sealant. The cell installation process was clearly described in our previous report [6]. Since LSCM electrode can operate in oxidizing or reducing atmospheres, hence recirculating part of the H_2 or CO arising from the electrolysis to provide reducing environment is not necessary. As shown in Fig. 1, the simulated flue gas was composed of CO_2, H_2O, SO_2, O_2, and balance gas N_2. The SO_2 concentration in CO_2 was 100 ppm. The humidifier was heated to provide a moisture content of 33% pH_2O balanced with CO_2, N_2, and O_2. The ratio of CO_2 to H_2O was controlled at 1:1. The total flow rate of flue gas that was fed into the fuel electrode was approximately 100 mL min^{-1}. The oxygen electrode side was exposed to ambient air. The line-heater connecting the humidifier to the SOEC was heated to more than 100 °C to prevent the condensation of steam in the pipe. The concentrations of SO_2 and O_2 that were fed into the fuel electrode varied from 0 ppm to 15 ppm and from 0% to 15%, respectively. Table 1 shows the flow rate of each flue gas component for the SOEC electrolysis.

The electrochemical performance of SOEC was characterized by using current density—voltage curves (I-V) and electrochemical impedance spectroscopy (EIS). The I-V curves were generated by using a galvanostat/potentiostat instrument (Solartron Model 1470 E) to control the voltage between 0 V and +2 V of bias against open circuit voltage (OCV) at a sweep rate of 2 mV^{-1}. The EIS measurements were performed by applying a 10 mV signal amplitude across a frequency range of 100 kHz to 0.1 Hz by using a frequency response analyzer (Solartron Model 1255 B). An X-ray diffractometer (XRD, Empyrean, PANalytical, The Netherlands) with a Cu Kα radiation source was employed to study the phase formation of LSCM and the possible interfacial reactions between LSCM and GDC. The microstructures of the cells before and after the