Sulfur dioxide removal from oxygen-rich exhausts by promoted decomposition

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Ta-Jen Huang *, Chih-Wei Mao, Cheng-Chin Lee, De-Yi Chiang, Chi Shih, Bo-Chung Wang, Shan-Yuan Lee, David Shan-Hill Wong

Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC

HIGHLIGHTS

- The electrochemical double-cell plates highly promote direct SO_2 decomposition.
- Sulfur vapor and gaseous oxygen are formed without consuming any reagent.
- SO_2 can be removed almost completely and sulfur can be recovered.
- A novel technology of promoted SO_2 decomposition is established.
- The real-world applicability is confirmed by an electro-catalytic honeycomb.

ARTICLE INFO

ABSTRACT

Sulfur dioxide (SO_2) is one major air pollutant from burning the fossil fuels and its easier and more effective treatment can offer better protection of human health. Here, we demonstrate that the electrochemical double-cell (EDC) plate highly promotes the decomposition of SO_2 in simulated oxygen-rich exhausts to sulfur vapor and gaseous oxygen without consuming any reagent or other resource. SO_2 can be removed almost completely. Sulfur can be recovered as solid after cooling the sulfur vapor. The $DeSO_2$ rate increases with SO_2 concentration and also with O_2 concentration. Highest $DeSO_2$ rate occurs at around 170 °C. A novel technology of promoted SO_2 decomposition (PSD) is thus established. The real-world applicability of PSD is confirmed by SO_2 removal from the boiler flue gas using the electro-catalytic honeycomb, which consists of numerous EDCs.

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1. Introduction

Since burning the fossil fuels for energy, the sulfur contained in the fuels to the engines, the boilers and other combustion processes is converted to sulfur dioxide (SO_2). This causes serious consequences on environment and human health. Thus, various methods of flue gas desulfurization (FGD) have been developed to remove SO_2 from the combustion exhausts. The most-widely-used SO_2 removal ($DeSO_2$) technology is limestone/gypsum wet FGD [1], which has high $DeSO_2$ efficiency, reliability and low utility consumption. However, it has drawbacks such as the supply and consumption of limestone powders as well as the production of byproduct gypsum needing disposal. Consequently, numerous regenerative processes have been devised. However, these disposal and regenerative processes are quite complicated and also need

quite large space. Therefore, they are not practical for the boilers of heating the buildings and the houses, especially in the metropolitan area where high sulfur-containing fuels are used. Consequently, the human health is still not well protected from SO_2 pollution for those people using the high sulfur-containing fuels such as coal for heating.

Direct reduction of SO_2 by CO or CH_4 to elemental sulfur has been reported over the ceria-based catalysts [2,3]. However, this reduction needs a temperature around 550 °C, which is much higher than that around 200 °C of the boiler flue gas after heat recovery. In these processes, the SO_2 molecule can undergo full dissociation into S and O adatoms [4,5] and it has been called SO_2 decomposition. Nevertheless, the O adatom formed needs a reducing agent to be removed from the catalyst surface; thus, such process should be SO_2 reduction but not direct SO_2 decomposition; in other words, SO_2 decomposition is only one step in the SO_2 reduction process.

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* Corresponding author. Tel.: +886 3 5716260; fax: +886 3 5715408.
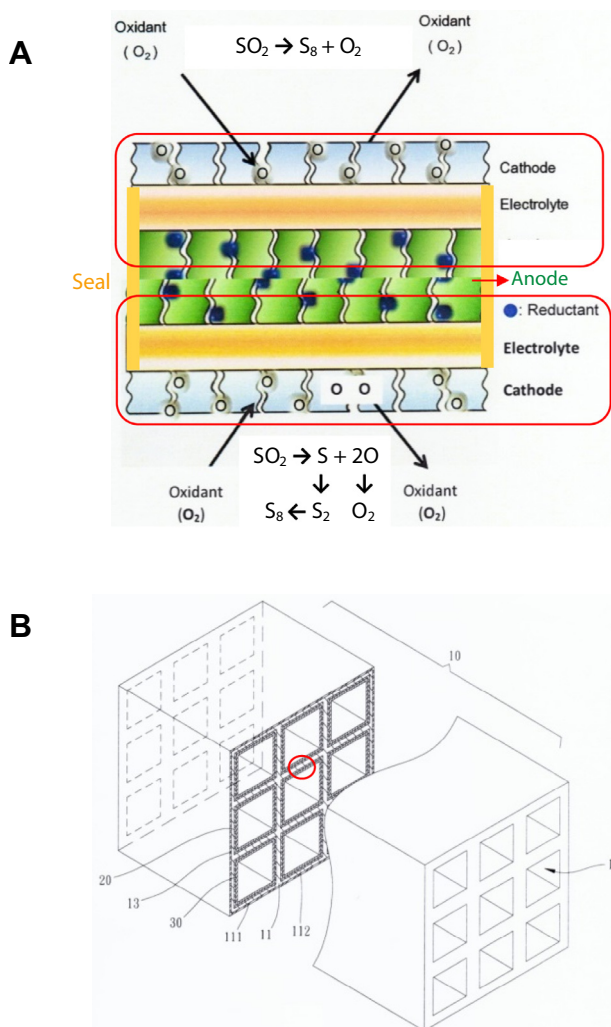*E-mail address:* tjhuang@che.nthu.edu.tw (T.-J. Huang).

Fig. 1. Schematics: (A) the electrochemical double-cell (EDC) plate and the $DeSO_2$ reactions. The red line-circled is an electrochemical cell. The EDC consists of two electrochemical cells, with each consisting of anode, electrolyte and cathode. The seal is to enclose the anode completely, in association with the dense electrolyte layers, so that the reducing potential of the anode can be maintained, with its importance discussed in the text. Note that the schematic of the EDC is the same as that of the EDC plate but without the seal. (B) The electro-catalytic honeycomb (ECH). The ECH consists of numerous EDCs, as red-line circled. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this work, we report SO_2 removal by direct decomposition of SO_2 to elemental sulfur and gaseous oxygen using the electrochemical double-cell (EDC) plates and a real-world device of electro-catalytic honeycomb, as shown in Fig. 1. The EDC plates are shown to be effective for real-world application, without consuming any reagent or other resource. Direct SO_2 decomposition is highly promoted over the cathode of the electrochemical cell of the EDC. A novel technology of promoted SO_2 decomposition (PSD) is therefore established. The real-world applicability of PSD is confirmed by SO_2 removal from the boiler flue gas using the electro-catalytic honeycomb.

2. Experimental details

2.1. Preparation of cathode composite materials

The cathode is made of the composite material of cathode catalytic material and gadolinia-doped ceria (GDC) powder ($Ce_{0.9}Gd_{0.1}O_{1.95}$, Fuel Cell Materials, Lewis Center, OH, USA). The

cathode catalytic material of $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ (LSM) was obtained from the Fuel Cell Materials (Lewis Center, OH, USA) in a form of LSM–GDC composite powder with LSM:GDC = 1:1 in weight. The cathode catalytic material of $(La_{0.8}Sr_{0.2})_{0.95}CoO_3$ ($L_{0.8}SC$) powder was also obtained from the Fuel Cell Materials. The cathode catalytic material of $La_{0.6}Sr_{0.4}CoO_3$ ($L_{0.6}SC$) was prepared in this work, with the preparation procedure detailed elsewhere [6].

In this work, the plate with the LSM–GDC composite as the cathode material is denoted as the LSM plate, that with $L_{0.6}SC$–GDC for the cathode is the $L_{0.6}SC$ plate, and that with $L_{0.8}SC$–GDC for the cathode is the $L_{0.8}SC$ plate. The $L_{0.6}SC$–GDC composite was prepared by mixing the $L_{0.6}SC$ powder and the GDC powder at $L_{0.6}SC$:GDC = 1:1 (w/w) with deionized water. The mixture was ground for 24 h and then dried. Then, the powder was calcined by heating to 500 °C and held for 2 h, and then to 900 °C, held for 2 h. The heating rate was also 5 °C min^{-1}. The powder sieved with 325 mesh screen was used as the cathode material. The $L_{0.8}SC$–GDC composite was prepared in the same way.

2.2. Fabrication of the EDC plate and the electro-catalytic honeycomb

In this work, the EDC plates were fabricated by two methods. The first method was to seal two commercial electrochemical cells (anode-supported, with LSM–GDC composite for the cathode layer and LSM for the cathode current collecting layer, Fuel Cell Materials, Lewis Center, OH) together and then to seal it as shown in Fig. 1 (A). The second method was to fabricate the anode also as the supporting plate, then to coat the electrolyte layer, the interlayer and the cathode layer successively on both sides of the plate, and then to seal it as in the first method. Notably, the interlayer is used to enhance the adhesion between the electrolyte layer and the cathode layer so that the calcination temperature of the cathode layer can be lowered [7]; however, it is not a basic component in the electrochemical cell and is thus not shown in Fig. 1(A). The $L_{0.6}SC$ and $L_{0.8}SC$ plates were fabricated only by the second method while the LSM plates by both methods; note that the LSM plate fabricated by the first method, which used the commercial cells, is denoted as the commercial LSM plate.

For fabricating the EDC plates by the second method, the anode was made of the composite material of NiO powder (0.5–1.5 μm, Fuel Cell Materials, Lewis Center, OH) and 8YSZ powder (8 mol% yttria-stabilized zirconia, 0.3–0.6 μm, Meitek, Taiwan) mixed at NiO:8YSZ = 3:2 (w/w). The electrolyte was made of 8YSZ powder (5–10 nm, Fuel Cell Materials, Lewis Center, OH). The interlayer was made of GDC. The cathode was made of LSM–GDC, $L_{0.6}SC$–GDC or $L_{0.8}SC$–GDC composite; the cathode loading was 0.021 g cm^{-2}, if not specified otherwise. The slurry for coating was made by mixing the powder with 30 wt.% methanol and stirring for 24 h.

In this work, an electro-catalytic honeycomb, as shown in Fig. 1 (B), was fabricated with the honeycomb monolith of 200 channels in^{-2}, i.e., a cell density of 200 cpsi (cells per square inch). The details of the fabrication procedure of the electro-catalytic honeycomb have been described elsewhere [8]. Before 1400 °C calcination after coating the electrolyte layer, the diameter of the honeycomb was 3.5 cm and its length was 5.8 cm. The cathode catalytic material was LSM–GDC composite with LSM:GDC = 1:1 in weight. The cathode surface, i.e., the treatment area, of the electro-catalytic honeycomb fabricated in this work is 347 cm^2.

2.3. Activity tests

The $DeSO_2$ activities were measured by putting an EDC plate in a rectangular glass tubular reactor so that a simulated exhaust could flow perpendicularly onto both cathode surfaces from both