



In-situ catalytic oxidation of Hg^0 via a gas diffusion electrode



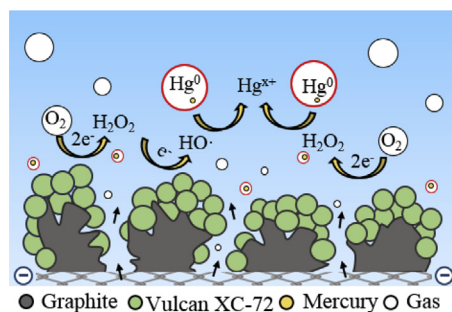
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HIGHLIGHTS

- A novel diffusion electrochemical reactor was proposed to remove Hg^0 .
- The reaction mechanism of Hg^0 removal was investigated.
- Hydrogen peroxide and hydroxyl radicals play a dominant role for Hg^0 removal.

GRAPHICAL ABSTRACT



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ABSTRACT

A diffusion electrochemical reactor was proposed to remove elemental mercury (Hg^0) from coal-fired flue gas. The experiments were carried out in an undivided column reactor with a self-made gas diffusion electrode (GDE) as cathode and Ti/IrO_2 as anode. Hg^0 was oxidized when the simulated gas passed through GDE. It turned out that the removal of Hg^0 in electrochemical process was dominated by electro-generated H_2O_2 and free radicals on GDE interface or in the electrolyte. Under 70 °C, Hg^0 removal efficiency exceeded 90% after 40 min electrolysis. The effects of operation parameters were investigated and the results demonstrated that voltage, gas flow rate, and initial concentration of Hg^0 had significant influences on Hg^0 removal, especially the reaction temperature, electrolyte concentration and pH. H_2O_2 and HO^\cdot in the electrolyte were measured by UV–vis spectrophotometer and electron spin resonance (ESR), respectively. The above results show that electrochemical technique is a promising method for emission control of Hg^0 from coal-fired flue gas.

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1. Introduction

Mercury, a hazardous air pollutant (HAP) as designated by US EPA, has received a considerable attention due to its high toxicity, long range transport, persistent and bioaccumulation [1]. It was estimated that about 2320 t of Hg was emitted to the globe atmosphere annually [2]. Coal combustion accounting for more than

60% of total mercury release, was regarded as the main source of mercury emissions to the atmosphere [3]. The mercury released to the environment can be converted through biological processes into methyl-mercury (Me-Hg), which is highly toxic and may cause neurological damage depending on its concentration in food or water [4]. Therefore, it is significant to control the emission of mercury to the atmosphere.

In the flue gas derived from coal-fired power plants, particulate mercury (Hg^p), oxidized gaseous mercury (Hg^{2+}) and elemental mercury (Hg^0) are the main forms. The Hg^p and Hg^{2+} can be effectively removed through particulate matter collection devices and

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wet flue gas desulfurization facilities, respectively. However, Hg^0 is difficult to be removed due to its high volatility and insolubility [5]. Hence, two main strategies are used to remove Hg^0 from flue gas: Hg^0 adsorption and oxidize Hg^0 to Hg^{2+} . The former technology is costly by injecting activated carbon [6] and novel sorbents [7] into the flue gas. The latter one includes the addition of strong oxidants like halogens, ozone or H_2O_2 to the flue gas [8], photochemical oxidation, using catalysts [9] or membranes with catalytic oxidation system [10]. However, some technical problems such as the application costs, safety, reliability and secondary pollution of reaction products can't be effectively resolved yet [11]. Therefore, the development of high efficiency, low pollution and economic technology is urgently needed nowadays.

Recently, the advanced oxidation technology has been widely studied to solve environmental problems. The highly active and non-selective hydroxyl radicals ($\text{HO}\cdot$) produced from H_2O_2 , UV/ H_2O_2 and metal/ H_2O_2 can oxidize many kinds of pollutants. So far, various reports are concerning the use of commercial H_2O_2 to remove Hg^0 from flue gas. Korell, J. et al. [12] applied H_2O_2 solution to oxidize Hg^0 to Hg^{2+} from the flue gas in the wet scrubber. Yangxian Liu et al. [11] remove Hg^0 from flue gas containing SO_2/NO by UV/ H_2O_2 process in a novel photochemical reactor. Nevertheless, the cost and hazards associated with the transport and handling of commercial concentrated H_2O_2 can't be neglected [13]. Moreover, a notable shortcoming exists in this chemical process is the fast consumption of H_2O_2 and the need of adding H_2O_2 continuously. The above problems can be solved if H_2O_2 can be generated in a simple system efficiently and continuously.

In recent decades, lots of researches have proved that H_2O_2 could be in-situ electro-generated by the two electron reduction of oxygen in an electrochemical system [14]. However, traditional cathode materials such as graphite felt and ACF are not efficient in H_2O_2 production due to the low solubility of oxygen. This limitation can be overcome when O_2 is supplied through gas diffusion electrode (GDE). It has been demonstrated that GDE can enhance H_2O_2 productivity due to its excellent electrical conductivity, high surface area and porous structures, leading to a faster reduction of oxygen. Moreover, the porous structures contain abundant hydrophobic channels, which enormously supply unlimited oxygen to the electrode/electrolyte interface rather than dissolve into the solution [15].

In these experiments, pure air containing mercury vapor was used as the simulated gas and it was diverted to GDE directly. GDE catalyzed the reduction of oxygen to produce H_2O_2 , which was from simulated flue gas without other pumped oxygen. The high concentration of electro-generated H_2O_2 was electro-activated and large amount of highly reactive radicals like $\cdot\text{OH}$ was produced. H_2O_2 and $\cdot\text{OH}$ existing in the electrolyte could oxidize Hg^0 directly and kept it in the solution when mercury vapor passed through the porous structure of GDE and the electrolyte. This is the design idea to convert Hg^0 by electrochemical process and with our effort, desirable results were achieved.

The innovative approach developed in our present work consists of investigating into the feasibility of using GDE for the in situ electro-generation of H_2O_2 and the indirect electro-oxidation of Hg^0 from flue gas in a well-designed electrochemical reactor. In current study, a Ti/IrO₂ anode and a self-made gas diffusion electrode as the cathode were used for the electrochemical oxidation of Hg^0 . The cooperative oxidation of electro-generated H_2O_2 with reactive oxygen radicals and active anode is supposed to increase the oxidation Hg^0 rate markedly. Sequences of experiments were investigated to explore the relevant operational parameters effect on H_2O_2 production as well as Hg^0 removal efficiency.

2. Experimental section

2.1. Chemical and materials

The carbon black powder (CB, Vulcan XC-72R) was purchased from Cabot Corporation and used without any further treatment. Graphite (Sinopharm Chemical Reagent Co., Ltd, China.) was pretreated: boiled in deionized water for 2 h, rinsed twice with deionized water, filtered with a filter, dried at 80 °C and then stored for later use. Polytetrafluoroethylene emulsion solution (PTFE, 301B, 60 wt%, Shanghai 3F New Materials Co., Ltd, China.) 5,5-dimethyl-1-pyrroline N-oxide (DMPO, ≥97%) was bought from Aladdin Chemical Reagent (Shanghai) Co., Ltd, China. Mercury permeation tube was purchased from Suzhou Qingan Instrument Co., Ltd, China. The commercial Ti/IrO₂ was purchased from Baoji Yichen Technology Co., Ltd, China. The loading of Ti/IrO₂ anode is 1 mg IrO₂ per cm².

2.2. Preparation of gas diffusion electrode (GDE)

The gas diffusion electrode was consisted of three parts: the stainless wire was employed as substrate, the graphite gas diffusion layer and carbon black (XC-72) catalyst layer. The fabrication procedure was as follows: 0.2 g pretreated graphite and 0.1 g carbon black (Vulcan XC-72) were added into 60 mL 3% ethanol in a conical flask, respectively. And the conical flasks were put in an ultrasonic bath for 15 min at room temperature, and then appropriate amount of PTFE was added into the mixtures and kept ultrasonic dispersion for another 15 min. Next, the mixtures were stirred at 80 °C until they became desirable flocks and the flocks were filtered on a circulate stainless steel wire in order to form a paste. The resulting paste was put into a mold to be pressed under 20 MPa for 3 min to form a circulate sheet (R = 22.5 mm, 1.7 mm thickness). Via calcination at 350 °C for 60 min, a GDE was fabricated.

2.3. Experimental apparatus

The experimental installations are consist of gas cylinder (purity, 99.99%), mass flow meter, water bath, mercury vapor generator (Suzhou Qingan Instrument Co., Ltd, China), self-designed reactor, direct current constant voltage power supply with current-voltage monitor, PC and mercury vapor analyzer (SG-921, Jiangsu Jiangfen Electro-analytical Instrument Co., Ltd, China.). All the reactions were carried out in an undivided self-designed column reactor with effective sectional area of 7.07 cm² and volume of 100 mL as shown in Fig. 1(a). Fig. 1(b and c) shows the Ti/IrO₂ anode and gas diffusion cathode, respectively. Mercury permeation tube was placed in a sealed U shaped glass tube which was immersed in a temperature controlled water bath. By adjusting the temperature of the water bath, Hg^0 Concentration in the simulated gas could be controlled. A laboratory direct current constant voltage power supply and current-voltage monitor was used to provide the electric power and detect the current. A continuous mercury analyzer was used to detect the inlet and outlet Hg^0 Concentration. Vent gases were treated with potassium permanganate saturated solution to avoid air pollution.

2.4. Electrolytic procedures

80 mL Na₂SO₄ solution was used as supporting electrolyte and the initial pH was adjusted by H₂SO₄ and NaOH. The prepared GDE (Section 2.2) was used as cathode and Ti/IrO₂ (R = 15 mm) as the anode. The distance between Ti/IrO₂ anode and GDE cathode was 10 mm. Pure air (21% O₂ with N₂ left) was used as oxygen

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