

Gas-phase electrocatalytic reduction of carbon dioxide using electrolytic cell based on phosphoric acid-doped polybenzimidazole membrane

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Abstract

Carbon dioxide transformation to fuels or chemicals provides an attractive approach for its utilization as feedstock and its emission reduction. Herein, we report a gas-phase electrocatalytic reduction of CO₂ in an electrolytic cell, constructed using phosphoric acid-doped polybenzimidazole (PBI) membrane, which allowed operation at 170 °C. Pt/C and PtMo/C with variable ratio of Pt/Mo were studied as the cathode catalysts. The results showed that PtMo/C catalysts significantly enhanced CO formation and inhibited CH₄ formation compared with Pt/C catalyst. Characterization by X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy revealed that most Mo species existed as MoO₃ in PtMo/C catalysts and the interaction between Pt and MoO_x was likely responsible for the enhanced CO formation rate although these bicomponent catalysts in general had a larger particle size than Pt/C catalyst.

Key words

carbon dioxide; gas-phase electrocatalytic reduction; platinum-molybdenum catalyst; Faradaic efficiency; formation rate

1. Introduction

Electrocatalytic reduction of carbon dioxide (CO₂) to fuels or chemicals provides an attractive strategy for both CO₂ emission reduction and energy storage. Coupling this process to electrical energy from intermittent renewable sources such as wind and solar energy can yield carbon-neutral fuels for use in stationary and transportation power [1,2]. Up to now, different kinds of electrolytic cells have been developed to explore CO₂ electrocatalytic reduction. At the temperature below 100 °C, usually at room temperature, electrolyte solutions such as KHCO₃ and H₂SO₄ solutions [3,4], in some cases together with ionic liquid [5,6], were used to assist the reduction of CO₂ on Sn, Cu, Au, Ag electrodes [7–9]. Formate [10], CO [11,12] and hydrocarbon [13,14] products were produced with a high Faradaic efficiency and energy efficiency. However, CO₂ solubility is limited in these electrolyte solutions, thus, large amounts of electrolyte solutions are essential during CO₂ reduction, which is a great challenge for further large-scale practical applications. High-temperature electrolytic cells have also been reported recently, such as solid oxide electrolytic cell [15], solid proton conductor electrolytic

cell [16] and molten carbonate electrolytic cell [17]. The operation temperature is between 400–700 °C, and CO, CH₄ and carbon are produced by a gas-phase reduction process.

Phosphoric acid-doped polybenzimidazole (PBI) membrane is a well-developed electrolyte for high-temperature proton exchange membrane fuel cell and steam electrolytic cell operating up to 200 °C [18]. Compared with electrolytic cell based on Nafion[®] membrane working below 100 °C, water can exist in gaseous form during the electrolysis process, which has some advantages such as lower reverse voltage and overpotential for water electrolysis and simple electrolytic cell structure free of cooling system from the thermodynamic, kinetic and engineering points of view. Until now, CO₂ electrocatalytic reduction in electrolytic cell based on phosphoric acid-doped PBI membrane has not been reported yet. In this work, we constructed electrolytic cell using phosphoric acid-doped PBI membrane to explore the gas-phase reduction of CO₂. PtMo/C catalysts were prepared by an impregnation-reduction process and employed as the cathode catalysts due to that CO₂ can be converted to CO on PtMo catalyst by reverse water gas shift reaction in proton exchange membrane fuel cell [19,20]. The prepared catalysts were characterized

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by X-ray diffraction (XRD), X-ray photoelectron microscopy (XPS) and transmission electron microscopy (TEM). Linear sweep voltammetry and electrocatalytic activity tests were performed to investigate the electrocatalytic reduction of CO₂ on PtMo/C catalysts as well as Pt/C catalyst for comparison.

2. Experimental

2.1. Catalyst preparation

Three PtMo/C catalysts with different nominal ratios of Pt/Mo were prepared in an impregnation process followed by a reduction treatment in 10% H₂/Ar atmosphere. Typically, a certain amount of ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Sinopharm Group) was dissolved in 20 mL water, and then commercial Pt/C catalyst (Tanaka Kikinzoku Kogyo, K. K., 40 wt% Pt) with a calculated amount was added into the solution with continuous stirring and dried at 60 °C. The powder was reduced in 10% H₂/Ar at 550 °C for 2 h. The prepared catalysts were denoted as PtMo/C-0.5, PtMo/C-1 and PtMo/C-2 according to the nominal atomic ratio of Pt/Mo of 0.5, 1 and 2, respectively.

2.2. Physicochemical characterization

X-ray diffraction (XRD) was performed on a Rigaku D/MAX 2500 diffractometer with Cu K_α radiation (λ = 1.5418 Å) at 40 kV and 200 mA. The scan speed was 2 °/min and the step size was 0.02°. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Scientific Escalab 250Xi spectrometer with Al K_α X-ray as radiation source. Pt (4f) and Mo (3d) signals were collected. The position of C (1s) peak, that is 284.6 eV, was used to correct the binding energies of PtMo/C and Pt/C catalysts. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G² microscope operated at an accelerating voltage of 120 kV.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in 0.1 mol/L K₂SO₄ (Sinopharm Group) solution in a 150 mL three-electrode cell (AKCELL3, Pine Research Instrumentation) at 25 °C. A commercial glassy carbon (GC) electrode (AFE5050GC, 5 mm in diameter, 0.196 cm², Pine Research Instrumentation) covered by the sample with Nafion[®] ionomer as a binder, Pt-wire electrode (Pine Research Instrumentation) and an Ag/AgCl electrode (Pine Research Instrumentation) in saturated KCl solution were used as a working electrode, counter electrode and reference electrode, respectively. The rotation rate and the potential of the working electrode were controlled by a MSR Electrode Rotator (Pine Research Instrumentation) and an Autolab potentiostat/galvanostat (PGSTAT 302N). 6 mg catalyst was dispersed in a mixture of 1 mL water, 1 mL ethanol and 50 μL Nafion[®]

solution (5 wt%, Dupont) with ultrasonic stirring to form a homogenous ink. The catalyst layer with a catalyst loading of 0.3 mg/cm² was prepared by dropping 20 μL of the ink onto a GC disk electrode by a micropipette and drying at room temperature. Linear sweep voltammeteries in Ar-saturated and CO₂-saturated 0.1 mol/L K₂SO₄ solution were conducted between -0.7 V and 0.2 V with a scan rate of 10 mV/s. The pH values of Ar-saturated and CO₂-saturated 0.1 mol/L K₂SO₄ solutions were measured to be 6.1 and 4.2. In order to obtain the same hydrogen evolution reaction (HER) activity on the catalysts in Ar and CO₂ atmosphere, the pH value of Ar-saturated 0.1 mol/L K₂SO₄ solution was adjusted to 4.2 with 0.05 mol/L H₂SO₄. Therefore, the current density contributed to CO₂ reduction on Pt/C and PtMo/C catalysts can be calculated by the difference on current density in Ar and CO₂ atmosphere. Ag/AgCl reference electrode was calibrated versus reversible hydrogen electrode (RHE) in H₂-saturated 0.1 mol/L K₂SO₄ solution (the pH value was also adjusted to 4.2 with 0.05 mol/L H₂SO₄) with platinum wire as the working electrode. All potential values in this paper were referred to RHE.

2.4. Membrane and electrode assembly (MEA) fabrication

A Toray carbon paper (Toray TGP-H-060, Toray Industries Inc.) was employed as the anode and cathode backing layers. Carbon black ink containing Vulcan XC-72 carbon black and polytetrafluoroethylene (PTFE) was painted onto the backing layer to form a microporous layer. The carbon black loading was about 0.5 mg/cm² and the PTFE content in the microporous layer was 15 wt%. PBI resin was dissolved in dimethylacetamide (DMAc) to form a 2 wt% solution, and polyvinylidene fluoride (PVDF) was dissolved in DMAc to form a 1 wt% solution. The prepared PtMo/C catalysts or commercial Pt/C catalyst was subsequently mixed with PBI and PVDF solutions. The resulting mixture was stirred for 12 h to form a catalyst ink (the weight ratio of catalyst, PBI and PVDF was 230 : 12 : 7). To fabricate the cathode catalyst layer, the catalyst ink was brushed onto the microporous layer at 85 °C. The catalyst loading in the cathode catalyst layer was 2.0±0.1 mg/cm². In all the cases, an identical anode catalyst layer was prepared by the same procedure as that described above. The resulting Pt black catalyst (Johnson Matthey Corp.) loading were 3.0±0.1 mg/cm², and the ratio of catalyst, PBI and PVDF was the same as that in the cathode catalyst layer. PBI membrane (FuMA-Tech GmbH, Germany) was doped with H₃PO₄ (85 wt%) at 70 °C for 24 h to obtain phosphoric acid-doped PBI membrane. Finally, the cathode and anode (5.2 cm×5.2 cm) were placed onto both sides of a piece of phosphoric acid-doped PBI membrane and hot-pressed at 145 °C and 0.2 MPa for 10 min to form MEA.

2.5. Electrocatalytic activity tests

MEA with two PTFE sheets was assembled into an electrolytic cell with stainless flow field plates and end plates. The electrolytic cell was installed on an in-house CO₂ electro-

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