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Electrochemical reduction of gaseous CO_2 with a catechol and polyethyleneimine co-deposited polypropylene membrane

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ABSTRACT

A novel solid polymer electrolyte was developed by co-deposition of catechol (CCh) and polyethyleneimine (PEI) on a polypropylene membrane for electrochemical reduction of CO_2 (ERC) in gas phase. ERC performance was both investigated in a gas-gas mode and a gas-liquid mode. The maximum CO production rate was 121 μmol/h and the faradaic efficiency was 51% in the gas-liquid mode, which were much higher than those obtained with AM-7001 under the same condition. The high loading rate of quaternary ammonium ions on the membrane and the large surface area provided by the porous nano-structure of the membrane contribute to the high ERC efficiency. Furthermore, the cost of the CCh/PEI-Q membrane was much lower than commercial Nafion membranes, endowing this novel composite SPE with great potential in industrial application.

1. Introduction

Electrochemical reduction of CO_2 (ERC) has attracted much attention since clean renewable energy can be used to drive CO_2 into chemicals. Over the past few decades, researchers have focused on developing catalysts for ERC in aqueous electrolytes [1–3]. However, much less attention has been paid to the innovation of electrolytes. Although different liquid electrolytes with good CO_2 solubility have been developed [4–6], using liquid electrolyte may lead to significant hydrogen evolution, difficulties in products separation and electrolyte leakage [7]. As an alternative, solid polymer electrolytes (SPEs) have been employed for ERC, due to their unique advantages including: 1) good mechanical strength and thermodynamic stability; 2) reduction of catalyst poisoning and electrode corrosion; 3) elimination of hydrogen evolution [7,8].

As the core part of an electrochemical membrane reactor, the SPE has significant impacts on CO_2 reduction products, faradaic efficiency and reduction efficiency. To obtain a better performance and desired reduction products, various sandwich type SPE/electrodes assemblies with different SPEs have been developed. Polycation-based anion-exchange SPEs could improve the ERC efficiency owing to the quaternary ammonium groups on the surface [8,9]. Verma et al. used AMI-7001 as the anionic SPE and Cu as the cathode catalyst; the obtained maximum efficiency was around 32% for CH_4 [8]. Electrochemical membrane reactors equipped with selemion [10] or metal-coated selemion [11] membranes were reported to achieve current efficiencies of over 90%. Despite the improved performance, polycation-based anion-exchange SPEs are prone to swell in aqueous solution or humidified environment [8]. Also, these SPEs do not have porous structures to provide more reaction sites [11,12]. Last but not the least, the high cost of the commercial polycation based anion-exchange membranes limits their practical applications. Consequently, the aim of this work is to prepare novel polycation-based anion-exchange SPEs using low-cost and porous membranes as substrates. Recently, surface deposition of bio-inspired polyphenolic coatings with dopamine or other precursors is becoming a versatile approach for membrane modification [13–15]. Phenolic-assisted co-deposition has also been demonstrated as an efficient way to incorporate functional groups in the coatings [16–19], which offers us the possibilities of developing desired SPEs.

Herein, we developed a polycation-modified anionic SPE with a polypropylene microporous membrane (PPMM) as the substrate. Quaternary ammonium groups were anchored onto the membrane via the co-deposition of catechol (CCh) and polyethyleneimine (PEI), followed by subsequent quarterization. This novel SPE was further fabricated into a SPE/electrodes assembly for ERC.

2. Materials and methods

2.1. Preparation of the CCh/PEI-Q membrane

CCh (10 mg/mL) and PEI (Mw = 600 Da, Aladdin, AP) with a mass ratio of 4:1 were dissolved in a Tris buffer solution (pH = 8.5, Sinopharm Co., Ltd., AP). The ratio of 4:1 was based on the results of our previous work studying the influence of the CCh/PEI ratio on the membrane performance [18]. PPMM with a porosity of around 75%, pore size of around 404 nm, was pre-wetted with ethanol and then immersed into the Tris buffer solution. The membranes were incubated for 5 h, rinsed with ultrapure water and dried in a vacuum at 40 °C. The

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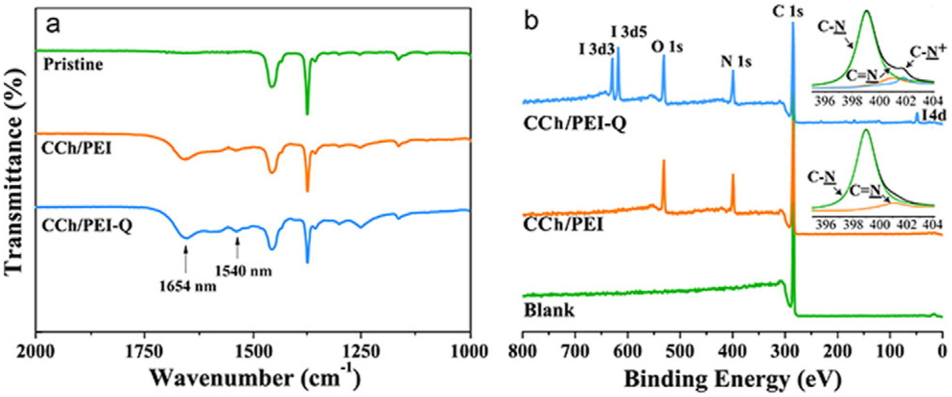

Fig. 1. (a) FT-IR/ATR and (b) XPS spectra of the CCh/PEI-Q membranes.

CCh/PEI modified membranes were further quaternized by a CH_3I/acetone solution (100 μL CH_3I in 30 mL acetone) to obtain the CCh/PEI-Q membrane. SPE surface morphologies were observed with FESEM (Hitachi S4800, Japan). FT-IR/ATR spectra were obtained by an infrared spectrophotometer (Nicolet 6700, USA) equipped with an ATR accessory (ZnSe crystal, 45°). XPS studies were performed on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA) with Al K radiation. Conductivity measurements were conducted with electrochemical impedance spectroscopy (Biologic VSP, France).

2.2. Electrode preparation

The microporous gas diffusion layer of the cathode was prepared by painting a mixture of PTFE emulsion, carbon black ink (Vulcan XC72R) on a piece of carbon paper (TGP-H-90, Toray Inc., Japan). Then 5 mg/cm^2 Ag nanoparticles was coated as catalysts. The anode electrode was prepared by coating 0.5 mg/cm^2 Pt/C catalyst ink (20%, Macklin Co., Ltd., China) on carbon paper. The morphologies of electrodes were observed with a SEM (SIRON-100, FEI, USA).

2.3. ERC reactor setup

The ERC reactor was a two-chamber electrochemical membrane reactor (15 mL for each chamber) with a SPE/electrodes assembly that was prepared by pressing a SPE between an anode and a cathode. The anode chamber was flushed with N_2 through a humidifier (gas-gas mode) or with 0.1 M Na_2SO_4 (gas-liquid mode). The cathode compartment for both modes was flushed with N_2 for 30 min, and then flushed with CO_2 (99.995%) through a humidifier for 1 h. Then constant current electrolysis was conducted using a potentiostat (Biologic VSP, France). All experiments were performed at 25 °C. The product was analyzed by a gas chromatograph (Fuli 9790, China) equipped with a methanizer.

3. Results and discussion

3.1. Characterization

Nano-sized CCh/PEI aggregates were deposited onto the surface, modifying the PPMM [18]. FT-IR/ATR analyses revealed new peaks at 1654 cm^{-1} and 1540 cm^{-1} for the modified membranes, representing the overlap of N—H bending vibration, C═C resonance vibration in aromatic rings or C═N stretching vibration within CCh/PEI aggregates (Fig. 1a). XPS spectra showed the peaks of O 1s and N 1s for the CCh/PEI co-deposited membranes and I 3d for the quaternized membrane (Fig. 1b). High-resolution N 1s spectra suggested the formation of C—N$^+$ bond for the CCh/PEI-Q membrane, demonstrating the successful CCh/PEI co-deposition and quaternization of PEI residues on the membranes. The amount of deposited quaternary ammonium groups were calculated at 0.23 mmol/g membrane.

The ionic conductivity of the fabricated SPE, indicating the transport ability of hydroxyl ions through the SPE, directly related to the ERC efficiency [20,21]. Fig. 2(a) showed the blank PPMM membranes had a very low conductivity of about 2×10^{-6} S/cm. The ionic conductivity increased significantly after the modification. The ionic conductivity of the CCh/PEI-Q membranes increased with the deposition amount of CCh/PEI nano-scale aggregates on PP membranes (Fig. 2b). Two reasons were responsible for the increase of ionic conductivity: 1) the increased amount quaternary ammonium cations on the SPE, which attracted loosely held hydroxyl groups and allowed them to exchange [9]; 2) the hydrophilic modified surface endowed the membrane with high water uptake (over 200%), which also increased the ionic conductivity (Fig. 2b) [8]. And it should be mentioned that no detectable swelling of the SPE occurred with such high water uptake, due to the robust polypropylene skeleton.

FESEM was used to characterize the morphology of the membrane surfaces. The unmodified PPMM membrane was white with a smooth surface. After the CCh/PEI co-deposition, the membrane became dark

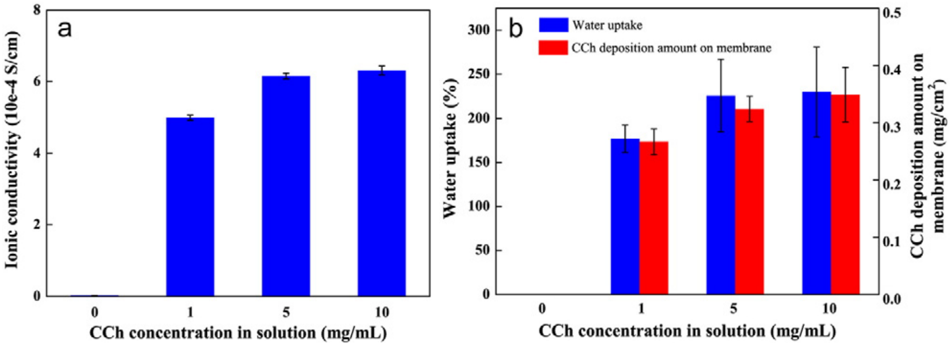

Fig. 2. (a) Ionic conductivity, (b) water uptake and deposition amount of CCh/PEI-Q SPEs and blank PPMM.