Supplementary information

Polymerized ionic liquid functionalized cathode catalyst support for

proton exchange membrane CO₂ conversion cell

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ESI 1. Material synthesis

Multi walled carbon nanotubes (MWNTs) were synthesized by a catalytic chemical vapor deposition method, where hydrogen decrepitated MmNi₃ alloy was taken as catalyst material. Here, acetylene was pyrolysed at 700 °C in argon atmosphere, which results in the growth of MWNTs on the surface of catalyst, called as-grown MWNTs. These as grown MWNTs were further purified by air oxidation followed by acid treatment to remove amorphous carbon and catalytic impurities.¹

The poly(ionic liquid) surface functionalized of MWNTs were synthesized as follows.² MWNTs (100.0 mg) was dispersed in dimethylformamide (DMF) (25.0 ml) by ultrasonication, followed by the addition of 200 mg of [VMIM]BF₄ and 7 mg of 2,2'-azobisisobutyronitrile (AIBN) under stirring. The mixture was transferred to a 50.0-mL round-bottomed flask equipped with a condenser and refluxed for 16 h at 80 °C under vigorous stirring and N₂ protection. Then the

reaction mixture was cooled down to room temperature and poured into 100 ml methanol in order to precipitate. The precipitate was washed with double-distilled water and methanol several times in order to remove physically absorbed polymer and unreacted monomer. Finally the reaction products were filtered through a nylon 66 membrane. The final product was dried in a vacuum oven at 60 °C and labeled as MWNTs-PIL.

The decoration of Pt nanoparticles over the surface of MWNTs and MWNTs-PIL was carried out by microwave assisted reduction method as reported.² Briefly, 50 mg of MWNTs or MWNTs-PIL was dispersed in 50 ml ethylene glycol followed by the drop wise addition of 2.77 ml aqueous solution of H₂PtCl₆.(H₂O)₆ (3.6 mg Pt in 1 ml solution). The solution was mixed thoroughly by stirring. The mixture was exposed to the microwave irradiation (800 W) for 2 min at 10 s pulse rate (5 s "ON" and 5 s "OFF") and then diluted with double-distilled water, filtered through a Nylon 66 membrane and washed with double-distilled water and acetone several times. The product with MWNTs support was labeled as Pt/MWNTs and with MWNTs-PIL was Pt/MWNTs-PIL.

ESI 2. Proton exchange membrane (PEM) CO₂ conversion cell fabrication

The construction of PEM CO_2 conversion cell is similar to that reported elsewhere, which mimics the conventional PEM fuel cell. The cell contains proton exchange membrane electrolyte, catalyst layers, gas diffusion layers, anode and cathode reservoirs and current collectors. Here, Nafion 117[®] proton exchange membrane was used as electrolyte, catalyst coated carbon cloth as cathode (or anode)-gas diffusion layer assembly. Carved channels on graphite plates are used as cathode and anode reservoirs while stainless steel plates are used as current collectors.



Figure S1: Schematic diagram of PEM CO₂ conversion cell. 1. Nafion electrolyte, 2. Electrodes (Anode and Cathode), 3. Currenr collector, 4. Anode reservoir, 5. Cathode reservoir, 6. Anode reservoir inlet, 7. Anode reservoir outlet, 8. Cathode reservoir inlet, 9. Cathode reservoir inlet.

The synthesized cathode electrocatalyst was dispersed in isopropanol by ultrasonic irradiation with 5 wt % Nafion[®] solution (50 wt% to the total electrode material) to produce a slurry. Cathode was made by coating the slurry on carbon cloth (11.56 cm², SGL Germany), which serves as gas diffusion layer as well, by simple brush coating technique. Anode also made in the similar route using commercially available Pt/carbon (Pt/C) with 20 wt% Pt loading was used as anode catalyst for catalytic water splitting. We maintained 0.5 mg/cm² Pt loading at cathode for all the experiments, unless otherwise mentioned.

Nafion® 117 membrane was sandwiched between the prepared anode and cathode at 130 °C with 2 ton load for 4 min. This membrane-electrode assembly (MEA) was further equipped with anode and cathode reservoirs to the respective sides. The electrical connections were given by stainless steel plates (fig S1).

ESI 3. Carbon dioxide conversion - Experimental procedure

Prior to the experiment, the cell was activated for 4 cycles of 15 min each applied potential of 1.5 V with deionized water in both reservoirs. High pure CO_2 (>99.9 %) was dissolved in deionized water by bubbling for an hour in order to maintain the partial pressure of CO_2 at 1 atm. Then the cathode reservoir solution was replaced with 40 ml of CO_2 saturated deionized water (CO_2 concentration: 33 mM i.e., 1.45 g/L @ 1 atm partial pressure, 25 °C) which was continuously circulated through the channels of graphite plates, while the anode reservoir still holds deionized water. Cathode reservoir was filled with CO_2 gas at 1 bar and sealed in order to maintain the initial equilibrium pressure at 1 bar. Cathode reservoir solution was circulated continuously by a peristaltic pump. The cell was powered with 1.5 V using a constant voltage power supply unit. The oxygen gas produced under applied potential was removed frequently by anode reservoir outlet. The cathode reservoir solution was sampled in certain period and analyzed using calibrated spectrophotometer.

The experiments were done in two modes:

- (i) Discontinuous Flow Mode (DFM): Here CO₂ was dissolved in deionized water upto 33 mM concentration (i.e., 1.45 g/L @ 1 atm partial pressure, 25 °C) and the solution was loaded in the tightly sealed cathode reservoir with 1 bar CO₂ equilibrium pressure. In this experiment, the dissolved CO₂ concentration decreases as it gets converted.
- (ii) Continuous Flow Mode (CFM): In this mode, CO₂ saturated deionized water was loaded in tightly sealed cathode reservoir in which CO₂ was bubbled, continuously in order to maintain the constant concentration.

To avoid the disturbance in cathode, we separated the bubbling chamber from cathode reservoir. CO_2 saturated deionized water was continuously circulated from bubbling chamber and the reacted solution at cathode reservoir was directed back to bubbling chamber using peristaltic pump.

ESI 4. Determination of formic acid concentration in cathode reservoir solution

The cathode solution was sampled in certain interval and analyzed by the calibrated spectrophotometer. The raw data of the absorption analysis in the wavelength range of 190 – 300 nm is presented in fig. for both Pt/MWNTs and Pt/MWNTs-PIL, in both discontinuous and continuous flow modes.



Figure S2. UV-Vis analysis data of cathode reservoir solution in DF mode (DFM) with Pt/MWNTs cathode electrode material.



Figure S3. UV-Vis analysis data of cathode reservoir solution in DF mode (DFM) with Pt/MWNTs-PIL cathode electrode material.



Figure S4. UV-Vis analysis data of cathode reservoir solution in CF mode (CFM) with Pt/MWNTs cathode electrode material.



Figure S5. UV-Vis analysis data of cathode reservoir solution in CF mode (CFM) with Pt/MWNTs-PIL cathode electrode material.

The obtained data from spectrophotometer was fitted to Gaussian function and determined the concentration of produced formic acid in the cathode reservoir solution by calibration curve.

ESI 5. References

- 1. M. M. Shaijumon and S. Ramaprabhu, *Chemical Physics Letters*, 2003, **374**, 513-520.
- 2. B. Wu, D. Hu, Y. Kuang, B. Liu, X. Zhang and J. Chen, *Angewandte Chemie International Edition*, 2009, **48**, 4751-4754.