Engineering hydrophobicity on anion exchange membrane for stable CO₂ electrochemical reduction in nonaqueous electrolyte

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Experimental

Materials

The following chemicals were purchased and used without further purification. Tetraethylammonium Perchlorate N(C₂H₅)₄ClO₄ (98%+, Adamas), Silver (Nano-powder, 99.9%, 50nm), QAPPT (5wt% in DMSO/acetone, Eve hydrogen Co. Ltd.), Pt mesh (Shanghai Chuxi Industrial Co. Ltd.), KOH (99.999%, Adamas), Dimethyl sulfoxide C₂H₆OS (99.7%, water \leq 50ppm, Adamas), Deionized water, PTFE filter (0.22 µm, 47 mm, Titan Scientific Lab), FAB-PK-130 (Fuma tech Co.Ltd.). All the electrochemical experiments were conducted in a H-cell (gaossunion Co.Ltd.) equipped with an Ag/AgCl reference electrode, controlled by an electrochemical workstation (CHI 760e).

Characterizations

The phase structure of the samples was confirmed by X-ray diffraction (XRD) at room temperature under ambient pressure, which was recorded on a Bruker D8 Advance operating at 40 kV and 40 mA with a Cu K α 1 radiation source ($\lambda = 0.154056$ nm) at a stepwise increase of 2 °·s⁻¹ in the Bragg angle (20) range from 5 ° to 80 °. The in-situ ATR-SEIRAS (attenuated total reflectance-surface enhanced infrared absorption spectroscopy) was carried out to investigate the intermediates and reaction mechanism of ECR with Bruker Vertex 70v FTIR spectrometer. Meanwhile, the *in-situ* SERS (surface-enhanced Raman spectroscopy) was applied to probe the reaction process. The wavelength of the excitation laser was 532 nm (the power was about 10 mW). Each Raman spectrum was recorded with 5 accumulations over an acquisition time of 12 s. The contact angle measurements were tested by depositing a small droplet on the surface using a syringe or pipette. Capture a side-view image of the droplet with a calibrated contact angle goniometer. Use the goniometer's software to analyze the image by fitting a curve to the droplet and calculating the contact angle at the point where the liquid meets the surface. Record the contact angle value and repeat the measurement several times to ensure accuracy. The ECR on Ag catalyst was performed in a home-made H-type *in situ* **Raman electrolysis** cell filled with CO₂-saturated 0.5 M TEAP/DMSO electrolyte. CO₂ was continuously bubbled into the electrolyte at a rate of 10 mL min⁻¹.

Electrochemical measurements

The catalyst ink was prepared by the following step, 8 mg Ag nano-powder and 50 µL QAPPT ionomer solution (5 wt%) was dispersed into 7.95 mL deionized water and isopropanol mixed solution. The catalyst was coated on a 1*1 cm carbon paper (TGP-H-060, Toray Industries, Inc.) by a spraying method and the loading mass was 1 mg/cm². All the electrochemical experiments were measured in a H-cell equipped with an Ag/AgCl reference electrode, controlled by an electrochemical workstation (CHI 760E). The working electrode and Ag/AgCl reference electrode (saturated KCl solution) were placed in the same compartment, while a platinum mesh counter electrode was placed in another compartment filled with 1M KOH solution. Between the two compartments, an anion exchange membrane was used as the separator. PTFE filters of varying diameters were tightly attached to the AEM where the hydrophobic side facing the anolyte. Prior to the ECR process, the CO₂ gas flow in the catholyte to exclude the dissolved other gas at the rate of 30 mL/min and lasted for the entire ECR process. The catholyte was forced stirred at the speed rate of 500 rpm. The electrochemical impedance spectroscopy (EIS) measurements were performed in a frequency range from 0.1 Hz to 100 kHz at a voltage amplitude of 5 mV at -1.5V vs Ag/AgCl. For the long-term ECR test in aprotic solution, the current was set as -10 mA in CO₂-saturated 0.5 M N(C₂H₅)₄ClO₄ DMSO solution. The stability was tested until the faradic efficiency of H₂ reached 10 %. LSV (linear sweep voltammetry) was carried out at a scan rates of 5 mV/s⁻¹ from -1 V to -2.5 V vs Ag/AgCl reference electrode. For the faradic efficiency analysis, the gas products were analyzed via an online gas chromatograph (Agilent 7890B), wherein TCD (thermal conductivity detector) and FID (flame ionization detector) were used to identify the H_2 and other gas products individually. Nuclear Magnetic Resonance (NMR) spectroscopy was utilized to quantitatively analyze the liquid-phase product, oxalate, generated during the reaction. Post-reaction liquid samples were collected and diluted in deuterated dimethyl sulfoxide (DMSO-d₆) with 0.1 mM tetramethylsilane (TMS) as an internal standard to ensure accurate chemical shift referencing and quantification. The oxalate anion was identified on a 600 MHz NMR spectrometer (AVANCE NEO 600) by its characteristic ¹³C NMR signal at approximately 158-160 ppm, corresponding to the carboxylate carbons.



Fig.S1 Contact angle measurements of (a) water and (b) DMSO on the PTFE filter.



Fig.S2 Electrochemical impedance spectroscopy (EIS) with different PTFE filter coverage.



Fig.S3 Mass of $KHCO_3$ precipitate collected in both chambers after 5 hours of chronopotentiometry electrolysis at 10 mA cm⁻² with varying PTFE filter coverage.



Fig.S4 The gas product signals tested by gas chromatograph.



Fig.S5 The liquid product signals tested by (a) 1 H NMR and (b) 13 C NMR.



Fig.S6 Digital photo of ATR-SEIRAS.



Fig.S7 *In situ* SERS spectra of ECR at the Ag surface in 0.5 M TEAP/DMSO solution saturated with CO₂. The arrow on the right shows the potential scanning direction. Peaks marked with black dashed lines are attributed to the reported SERS signals. All potentials are given vs AgCl.



Fig.8 (a) Digital photos of precipitation on the ion exchange membrane; (b) XRD pattern of the white precipitation and the standard pdf card of KHCO₃.