Supporting Information

Cobalt-Bridged Ionic Liquid Polymer on a Carbon Nanotube for Enhanced Oxygen Evolution Reaction Activity

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Removal of amorphous carbon and residual metal on CNT:

CNT produced by Shandong Dazhan Nano Materials Co. is multi-walled CNT with average diameter around 10 nm. The first step is washing it with nitric acid: 20 g of MWCNT were mixed with 1000 ml of acid (68%), stirred and heated up under reflux at around 100 °C for 20 h. After the reaction the gaseous supernatant was purged with nitrogen to remove acidic vapor for better handling. The material was filtered and washed extensively in a washing cell over night with distilled water to remove residual acid and impurities like iron. After that, the black wet CNT was dried in drying oven at 100 °C for 20 h. The as-obtained CNT powder then was annealed in furnace at 1000 °C for 20 h (argon condition). After all these procedures, we assume that the impurities on the pristine CNT have negligible influence for the further steps.

Synthesis of Co$_3$O$_4$/CNT

50 mg the pre-cleaned CNT were dispersed in 2 mL iso-propanol and sonicated for 5 min to get a good dispersion. 50 mg commercial Co$_3$O$_4$ (99.5%, Sigma-Aldrich) was dispersed in 1 mL H$_2$O and sonicated for 5 min. Then the two well dispersed materials were mixed together. The mixture was sonicated until solvents were all removed (no liquid phase can be observed). The as-obtained wet Co$_3$O$_4$/CNT then was transferred and dried at 80 °C overnight to get the final product.

Synthesis of SSPIL

SSPIL was synthesized with thermal-initiation free radical polymerization method from IL monomer 1-butanesulfonate-3-vinyl imidazolium hydrogen sulfate (SSIL 99%, Shanghai Chengjie Chemical Co., Ltd). Temperature programmed annealed processes were carried out according to the following procedures: annealing the IL precursor from room temperature to 40 °C (Argon, 20 min), maintaining for 5 h to remove the air in the furnace tube; then heating it to the 190 °C in 60 min, maintaining for 20 h.

Synthesis of SSPIL/CNT

36 mg IL precursor was solved in 1 mL water and 50 mg CNT was dispersed in 3 mL iso-propanol (IPA). Two solutions then were mixed and stirred until the solvent was removed. The polymerization process used the same procedure with SSPIL.

Synthesis of CoSSPIL/CNT series

50 mg CNT was firstly dispersed into 3 mL IPA by sonication. 14 mg cobalt carbonate (99.9%, Sigma-Aldrich) and 36 mg IL precursor (the molar ration of Co and IL is around 1:1 with a little bit
excess IL) was mixed in 1 mL water and heated to react for 60 min. The mixture was dropwisely added into the CNT IPA mixture. The mixture was stirred until the solvent was totally removed. Then the dried black hybrid was removed to small quartz boats which were placed in the center of a larger alumina tube running through the center of a furnace. Temperature programmed annealed processes were carried out according to the following procedures: annealing the hybrid from room temperature to 40 °C (Argon, 20 min), maintaining for 5 h; then heating it to the 190 °C in 60 min, maintaining for 20 h. The final products were obtained and named as CoSSPIL/CNT (CoSSPIL/CNT -1, the number 1 denoted the molar ratio of Co and IL precursor). Other samples CoSSPIL/CNT-0.5, CoSSPIL/CNT-1.5, CoSSPIL/CNT-2 and CoSSPIL/CNT-2.5 are obtained under same conditions with only varied IL precursor to18 mg, 54 mg, 72 mg and 90 mg, respectively.

Pretreatment of electrodes

Working electrode is 5 mm Ø glassy carbon (GC) disk electrode in PEEK sheath. Proper electrode pretreatment to get a mirror-like surface is done before every measurement. Before the first use, electrodes are sandpapered with decreasing roughness. Electrodnes are polished with polishing paste (Al₂O₃ slurry; 1.0 μm and 0.05 μm) on a wet polishing cloth for 3-5 minutes, and rinsed thoroughly with water. No scratches are visible on the glassy carbon surface. Before drop-coating of catalyst, electrodes are ultrasonicated in absolute ethanol for 5 minutes, rinsed thoroughly with water, ultrasonicated in millipore water for 5 minutes, rinsed thoroughly with water and dry in oven at 60 °C.

Ink preparation

Ink consists of 4 mL IPA, 960 μL H₂O and 40 μL Nafion solution (binder) and 5 mg sample. The catalyst is dispersed in the solvent by 15 min of ultrasonication. Proper dispersion yields a well dispersion without obvious particles. The catalyst precipitates from the dispersion over time. If any black precipitate can be seen, ultrasonication is repeated. The ink is used as soon as possible after been taken out from the ultrasonic bath.

Dropcoating

Electrodes with 50μg/cm² loading were produced. Volumes of 5 μL (twice) are pipetted onto the pretreated GC electrodes at room temperature and dried for 0.5 hours at 60 °C with a light uniform film formed on the electrode surface.

Electrochemical procedure

Electrochemical measurements comprise conditioning of work electrode, measurement of the open circuit potential (OCP), impedance spectroscopy (determination of iR-drop), cyclic voltammetry (CV,
“activity”) and constant-potential chronamperometry (CA, “stability”). All the procedures are done in 0.1 M KOH.

**Conditioning**

This part of the procedure consists of the determination of the open circuit potential (OCP) for 60 s and a subsequent linear sweep from the OCP to 1 \( V_{\text{RHE}} \) (5 mV/s) to avoid a harsh potential jump and stress on the working electrode. Conditioning is done by 30 cycles at 100 mV/s from 0 \( V_{\text{RHE}} \) to 1 \( V_{\text{RHE}} \).

**Impedance spectroscopy (determination of iR-drop)**

The uncompensated resistance (Ru, iR-drop) of the system is determined by electrochemical impedance spectroscopy (EIS) at the OCP. The first step is the determination of the OCP (for 60 s). EIS is carried out at the OCP: 25 data points between 100 kHz and 10 Hz with an amplitude of 10 mV\text{RMS}.

**Cyclic voltammetry (“activity measurement”)**

The cell remains switched on after EIS and the potential is swept from the OCP to 1 \( V_{\text{RHE}} \) (5 mV/s). Before start of the CV, the electrode is set to rotate at 1600 rpm. Cyclic voltammetry is conducted from 1 \( V_{\text{RHE}} \) to 1.8 \( V_{\text{RHE}} \) at 5 mV/s with automatic iR-compensation using Ru from impedance spectroscopy.

**Chronoamperometry (CA)**

To perform a stability test in chronoamperometric mode, the potential is kept at 1.8 VRHE after stationary polarization for two hours.

**XRD and Electrochemistry test**

X-ray diffraction patterns were recorded in Bragg-Brentano geometry on a Bruker AXS D8 Advance II theta/theta diffractometer, using Ni filtered Cu K\( \alpha \) radiation and a position sensitive energy dispersive LynxEye silicon strip detector at a scanning rate of 41.2\(^\circ\)/min. The electrochemical measurements were conducted in a three electrode system, which was controlled by using a potentiostat/galvanostat (BioLogic VSP, France). A platinized Pt wire as a counter electrode and a reversible hydrogen electrode (RHE, HydroFlex, Gaskatel GmbH) as a reference electrode were used.
Figure S1. Relevant S2p core level spectra of the IL/CNT and PIL/CNT. To confirm the interaction between PIL and CNT, IL/CNT and PIL/CNT were synthesized by combining IL and CNT at a higher ratio (2:1, IL/CNT) and followed by polymerization process at 190 °C (PIL/CNT).

IL/CNT and PIL/CNT samples were investigated as pressed pellets. XPS spectra were recorded using non-monochromatized Al Kα (1486.6 eV) excitation and a hemispherical analyzer (Phoibos 150, SPECS). The binding energy scale was calibrated by the standard Au4f(7/2) and Cu2p(3/2) procedure. +5V and -5V bias was applied to the samples, to understand whether or not all spectral features undergo the rigid shift. Spectral acquisition was carried out in standard (sample grounded) state and also upon applying positive and negative 5V bias.

Figure S2. Schematic illustration of the fabrication process of the PIL/CNT. During the polymerization process, part of the IL anion can react with CNT form some new sulfonate. This chemical bonding makes the PIL more stable on CNT surface and also ensures a good conductivity of the whole material during electrochemistry measurements.
Figure S3. Full range ATR-IR spectra of the IL monomer and the polymerized IL. ATR-infrared was performed on a fourier transform infrared spectrometer (Thermo Scientific® Nicolet iS50).

The polymerization process is also tested by nuclear magnetic resonance spectroscopy (NMR). Due to the limitation of the S element in NMR, we chose a BF4- as IL anion. Both 1H and 13C spectra of different samples show the polymerization process is well proceeded. The synthesis time was chosen to be 20 h to allow a complete polymerization. The unreacted free IL content is supposed to be very low.

Figure S4. NMR result of polymerized IL on CNT. Each sample is measured with NMR of 1H, 13C (IL neat in liquid phase; PIL and PIL/CNT in solid phase). All samples were measured on a 400MHz NMR magnet in a 1.3mm MAS Probe. IL was measured static while the PIL and PIL/CNT were measured at 20kHz.
Figure S5. C1s XPS spectra of SSPIL/CNT, CoSSPIL/CNT-0.5, CoSSPIL/CNT-1 (CoSSPIL/CNT) and CoSSPIL/CNT-1.5.

Figure S6. XRD pattern of the CoSSPIL/CNT. The main peaks of the sample can be all attributed to CNT.
Figure S7. Possible coordinated environment of the Co species with sufficient IL ligands.

Figure S8. EIS at the open circuit potential (OCP) of different samples. The first step is to determine the OCP. EIS is carried out at the OCP: 25 data points between 100 kHz and 10 Hz with an amplitude of 10 mV.
Table S1. The key performance indicators (KPI) of electrochemistry data of CoSSPILCNT-1 sample.

| name         | μg catalyst | geometric area | Electrolyte, PH | Protocol                  |
|--------------|-------------|----------------|-----------------|--------------------------|
| CoSSPILCNT   | 10          | 0.19625 cm²    | 0.1 M KOH, 13  |                          |
| OCP          | Ru          |                |                 | Initial EIS measurement  |
| 0.924 V<sub>RHE</sub> | 35 Ω    |                |                 |                          |
| E<sub>2mA/cm²</sub> | E<sub>5mA/cm²</sub> | E<sub>10mA/cm²</sub> | Initial activity measurement |
| 1.60 V<sub>RHE</sub> (auto iR-drop) | 1.62 V<sub>RHE</sub> (auto iR-drop) | 1.64 V<sub>RHE</sub> (auto iR-drop) | Mass activity in mA/μg |
| J<sub>m,1.6V</sub> | J<sub>m,1.7V</sub> | J<sub>m,1.8V</sub> |                 |                          |
| 0.020        | 0.17        | 0.37           |                 |                          |
| J t=0 h      | J t=0.5 h   | J t=2 h        | Stability at 1.8 V<sub>RHE</sub> |
| 16.3 mA/cm² | 20.2 mA/cm² | 19.9 mA/cm²    |                 |                          |
| OCP          | Ru          |                |                 | Second EIS measurement   |
| 0.901 V<sub>RHE</sub> | 35 Ω    |                |                 |                          |
| E<sub>2mA/cm²</sub> | E<sub>5mA/cm²</sub> | E<sub>10mA/cm²</sub> | Second activity measurement |
| 1.61 V<sub>RHE</sub> (auto iR-drop) | 1.63 V<sub>RHE</sub> (auto iR-drop) | 1.66 V<sub>RHE</sub> (auto iR-drop) | Mass activity in mA/μg |
| J<sub>m,1.6V</sub> | J<sub>m,1.7V</sub> | J<sub>m,1.8V</sub> |                 |                          |
| 0.020        | 0.15        | 0.32           |                 |                          |

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\text{TOF (µ = 400 mV)} = \frac{\text{Current/A}}{\text{Molar active sites}} = \frac{1.17 \text{ mA/A} \times 96485 \text{ S A/mol}}{0.0106 \mu \text{ mol}} = 0.29 \text{ s}^{-1}
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Figure S9. CV of different samples by dividing geometric area of the active electrode area. CV is conducted from 1 $V_{\text{RHE}}$ to 1.8 $V_{\text{RHE}}$ at 5 mV/s without automatic iR-compensation.

Figure S10. CV of pure CNT and different CoSSPIL/CNT series. Different numbers denote different IL monomer/Co molar ratio before polymerization process. CV is conducted from 0 $V_{\text{RHE}}$ to 10 $V_{\text{RHE}}$ at 100 mV/s. The increase of the IL will decrease the BET surface area; the more IL content the composite contains, the lower BET surface area it bears, thus explaining the lower capacitance. The 30 cycles conditioning process (between 0 $V_{\text{RHE}}$ to 1 $V_{\text{RHE}}$) can also avoid a harsh potential jump and stress on the working electrode.
Figure S11. CV of CoCO$_3$ and different CoSSPIL/CNT series. Different numbers denote different IL monomer/Co molar ratio before polymerization process. CV is conducted from 0.8 V$_{RHE}$ to 1.4 V$_{RHE}$ at 100 mV/s. The relative oxidation peak of CoCO$_3$ cannot be observed due to the high resistance and relatively low capacitance.

Figure S12. EIS at the open circuit potential (OCP) of CoSSPIL/CNT samples. Different numbers denote different IL monomer/Co molar ratio before polymerization process.
Figure S13. CV of different samples by dividing geometric area of the active electrode area and the content of Cobalt. CV is conducted from 1 $V_{\text{RHE}}$ to 1.8 $V_{\text{RHE}}$ at 5 mV/s without iR-compensation. Different numbers denote different IL monomer/Co molar ratio before polymerization process.

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