Electronic supplementary information (ESI)

Facile synthesis of Nafion-stabilized iridium nanoparticles and its direct use for fuel cells and water electrolyzers

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Characterizations of catalysts

The solvent of the Nafion-Ir colloid solution after dialysis treatment was evaporatd at 60 ºC to obtain solid sample for XRD test. And the XRD analyse was performed using a Philips CM-1 Power diffractometer with a CuKα radiation resource to determine the crystalline structure of the sample. The morphology of the catalysts was characterized with a TECNAI Spirit electron microscope operated at 120 KV. 300 metal nanoparticles (NPs) were calculated to obtain the particle distribution.

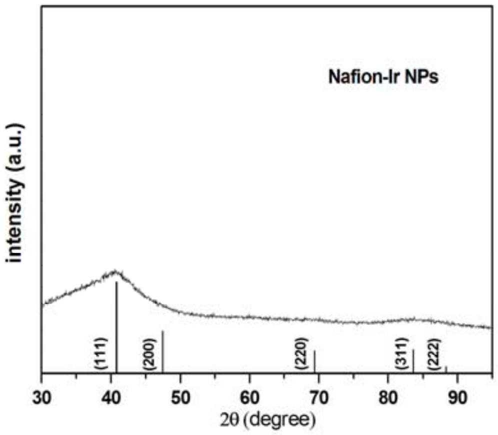

Fig. S1 XRD patterns of the prepared Nafion-Ir NPs

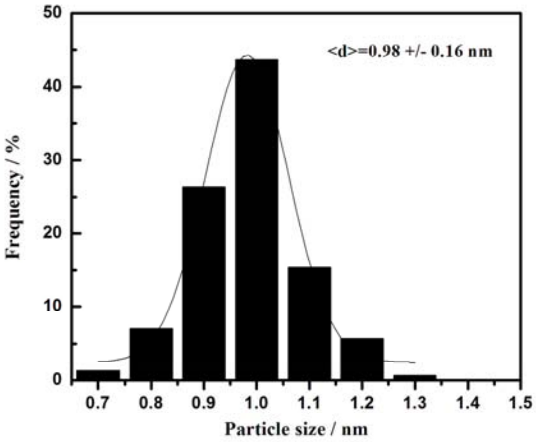

Fig. S2 Size distribution of the prepared Nafion-Ir NPs

Electrochemical characterizations

Electrochemical characterizations were performed on CHI 660 electrochemical station (CH Corporation, USA) with a rotating disk electrode (RDE) system (EG&G model 636). A standard three-electrode electrochemical cell was used. A large-area Pt foil (3 cm^2) and a saturated calomel electrode (SCE) served as the counter and the reference electrode, respectively. The catalyst layer on the glassy carbon electrode (GCE) (4 mm in diameter) was prepared as follows. 5 μl colloid solution after dialysis treatment was spreaded on the surface of the GCE and the electrode was dried in the air to obtain a thin catalyst layer. The weight concentration of Nafion-Ir in colloid solution was measured as follows: 1 ml colloid solution after dialysis treatment was added to a beaker and dried in the air, and then the beaker was transferred to a vacuum oven. The experiment was repeated for three times to get an average weight change of the beaker, and the concentration of the Nafion-Ir was obtained, 4.5mg Ir/ml in this work.

The electrochemical measurements were conducted in 0.5 M H_2SO_4 solution at room temperature.

1). **The Cyclic voltammograms (CVs) test for electrochemical active surface area (S_{EL}):**

CV data was recorded in the potential range of 0 to 0.75 V (vs NHE) at 50 mV s^{-1} after bubbling high-purity nitrogen through the electrolyte for 30 minutes. The S_{EL} was calculated as: $S_{EL} = Q_H/(Q_{ref} \times \text{Ir loading})$. Through integrating the $H_{a/d}$ peaks, the charge value (Q_H) was obtained, and $Q_{ref} = 0.22$ mC cm^{-2}.

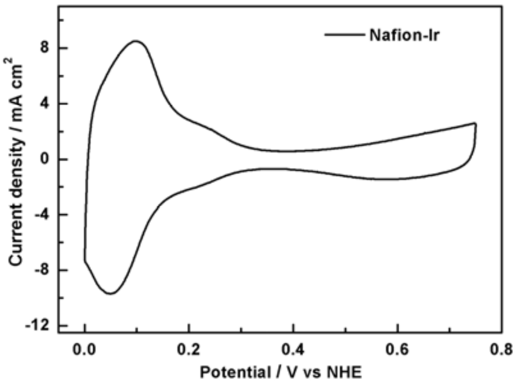

Fig. S3 The CV curve of Nafion-Ir for S_{EL} test

2) Activity for oxygen reduction reaction (ORR) tests

Pt black (T.K.K. Corp.), Nafion-Ir/C (weight ratio, Ir : C=50 : 50), and Pt/C (47.6 wt.%, T.K.K. Corp.) were mixed with Nafion (weight ratio, metal : Nafion=22 : 100 for Pt black and metal : total Nafion=1 : 1 for supported catalyst) and dissolved in 1 ml isopropanol. The metal concentrations of all the samples were equal to that of the Nafion-Ir colloid solution (4.5 mg/ml), and the catalyst layer on GCE were prepared same to that for Nafion-Ir.

The polarization curves for ORR on all the samples were obtained in O_2-saturated 0.5 M H_2SO_4 at 5 mV s^{-1} and 1600 revolutions per minutes (rpm).

3) Activity and durability for oxygen evolution reaction (OER) tests

IrO_2 prepared by Adams method was used as comparison, and the catalyst layer on GCE was prepared same to that for Pt black. The Ir loadings of the two samples on the GCE were the same. All the tests were performed in N_2-saturated 0.5 M H_2SO_4 solution.

For Nafion-Ir, anodic oxidation of Ir was performed with the potential scanned between 0 and 1.45 V (vs NHE) at 50 mV s^{-1} until the CV curve becomes constant. After that, the activity and durability for OER tests were performed.

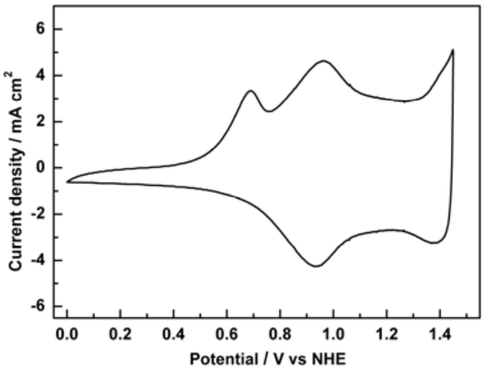

Fig. S4 The CV curve of Nafion-Ir after anodic oxidation process

The polarization curves for OER on all the samples were obtained with potential scanned from 1.05 to 1.6 V (vs NHE) at 5 mV s^{-1}. The durability test of the Nafion-Ir was conducted with potential scanned between 0.25 and 1.45 V (vs NHE) for 500 cycles.

Preparation processes of membrane electrode assemblies

The gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs) are fabricated as follows. The mixture of Pt/C (28.4 wt.%, T.K.K. Corp.) and Nafion using wasopropanol as the solvent was sprayed onto the gas diffusion layer (GDL) to form the GDE of the hydrogen electrode with a loading of 0.2 mg Pt cm^{-2}. The colloid solution after dialysis treatment was sprayed onto the GDL to form the GDE of the oxygen electrode. Then the Nafion 212 membrane was sandwiched between a hydrogen and a oxygen GDE, then a hot treatment was performed at 160 ^{o}C under 1 MPa for 1 minute to obtain MEAs. Moreover, the Nafion® content was 25% for hydrogen electrode.

For the supported Nafion-Ir/C, the preparation procedure of the oxygen electrode was as follows: The mixture of Nafion-Ir/C and Nafion using isopropanol as the solvent was sprayed onto the GDL to form the GDE of the hydrogen electrode with a loading of 0.5 mg Ir cm^{-2}, and the weight ratio of Nafion-Ir/C to Nafion was 3:1.

Operation conditions and cell performance measurements

The cell performance with a 5 cm^2 electrode area was determined as described in a previous paper.[1] As fuel cells, the cell was operated at 80 ^{o}C with H_2/O_2 at pressure of 0.2 MPa. The reactant gases, hydrogen and oxygen, are externally humidified before entering the test cell by bubbling them through the water at 90 ^{o}C and 85 ^{o}C respectively. As water electrolyzers, deionized water was pumped into the oxygen electrode from water reservoir kept at 80 ^{o}C at atmospheric pressure. The polarization curves of the cell are galvanostatically measured at constant current.

1. Zhi-Gang Shao, Baolian Yi, Ming Han, J. Power Sources, 1999, **79**, 82.