Supporting information

Carbon oxidation reactions could significantly misguide the evaluation of carbon black-based oxygen-evolution electrocatalysts

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Experimental

Synthesis of Fe-N-C: The Fe-N-C catalyst was synthesized according to the reported literature.¹ Typically, 2 mL aniline was firstly dissolved in 0.5 M HCl with Ketjenblack EC300 treated with 70% HNO₃ as the support. 4 g APS dissolved in 0.5 M HCl was added slowly to the solution and kept at $0\sim5$ °C for 8 hours to obtain PANI. Then the solution was filtrated and washed with water for 3 times. The PANI was dispersed in water again with FeCl₃·6H₂O added. Then the mixture was vacuum dried with rotary evaporator. The obtained powder was pyrolyzed at 900 °C for 1 h and washed in 0.5 M H₂SO₄ for 8 hours. Finally, the catalyst was heated again at 900 °C for 2 hours.

Electrochemical measurement: The catalyst "ink" was prepared by dispersing 5 mg EC600 in 1 mL isopropanol without adding Nafion ionomer to avoid the disturbance of sulfonic acid group. After ultrasonication, 5 μ L of the "ink" was deposited onto the gold electrode (5 mm in diameter). The oxygen evolution reaction was conducted in a three electrode cell through linear sweep voltammetry in 1 M KOH at a potential range of 1.1-1.7 V (vs. RHE) with a scan rate of 5 mV s⁻¹. No ohmic correction was carried out for evaluating the activity of OER. The EC600 after OER test (denoted as O-EC600) was collected from the gold electrode, washed several times with pure water and dried for further characterization. The OER test for Fe-N-C is the same as EC600.

Characterization: The contact angle of water droplets on EC600 and O-EC600 were tested to prove the surface change after OER test. The catalyst was first grinded thoroughly to get a fine powder. Several drops of isopropanol were then added to the powder to get a slurry, which was casted on the surface of a flat glass and press tightly to get a dense and flat surface for the contact angle test. The content of oxygen on the surface of the carbon catalyst was determined by X-ray photoelectron spectroscopy (Kratos Ltd. XSAM-800 equipped with an Al K α X-ray source). For XPS, the binding energies were calibrated to the C 1s peak at 284.3 eV and the data are fitted with the public software XPSPEAK. The structure and morphology of EC600 was characterized by Transmission Electron Microscope (TEM, JEM-2100F).



Figure S1. The TEM image of EC600



Figure S2. Polarization curves (without IR correction) of a commercial IrO_2 sample without carbon support in 1 M KOH at potential scan rate of 5 mV s⁻¹. The catalyst loading is 125 μ g/cm².



Figure S3. The device for quantifying the produced O_2 .

The produced oxygen was quantified through the following equipment. First, the electrolyte was saturated with oxygen to prevent the dissolving of oxygen from the OER catalyst. Seal the vessel instantly after bubbling into the electrolyte for 30 min. A small drop of water was injected into the glass tube (inner diameter =0.1 mm) and mark the position of the water drop. By measuring the distance the water drop moved, the volume (V) of the evolved oxygen can be determined. The faradaic efficiency (F) is calculated through the following equation:

$$F = \frac{V/V_0 \times n \times N_A \times e}{q} \times 100\%$$
 (S1)

 V_0 is the volume of 1 mol of gas under standard condition, *n* is the electrons consumed to produce an O₂ molecule, N_A is the the Avogadro's number, *e* is the charge of a electron, q is the total charge of the OER test. The distance is measured to be 1.3 cm in this test. Thus the faradaic efficiency is calculated to be 2.78 %.



Figure S4. (a) OER Polarization curves of Fe and N doped carbon catalyst (Fe-N-C) in 1 M KOH at a scan rate of 5 mV s⁻¹ (no IR-correction). (b) XPS high resolution O 1s spectroscopy for Fe-N-C and Fe-N-C after the OER test.

Notes and references

1. G. Wu, K. L. More, C. M. Johnston and P. Zelenay, *Science*, 2011, **332**, 443-447.