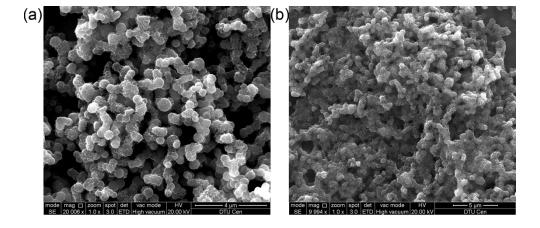
## **Supporting Information**

**Title:** Fe<sub>3</sub>C-based Oxygen Reduction Catalysts: Synthesis, Hollow Spherical Structures and Applications in Fuel Cells

Author(s): Yang Hu, Jens Oluf Jensen, Wei Zhang, Santiago Martin, Régis Chenitz, Chao Pan, Wei Xing,\* Niels J. Bjerrum and Qingfeng Li\*



**Fig. S1** SEM images of (a) Fe/C-630 and (b) Fe<sub>3</sub>C/C-660.

Sample	Mean diameter
Fe/C-500	412 nm
Fe/C-600	408 nm
Fe/C-630	448 nm
Fe/C-660	436 nm
Fe/C-700	445 nm
Fe/C-800	530 nm

Table S1 Mean diameters of the spheres of prepared catalysts.

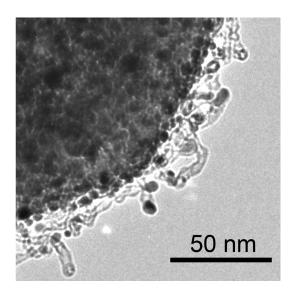


Fig. S2a CNT structures on the surface of a Fe/C-700 catalyst sphere.

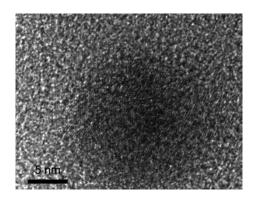
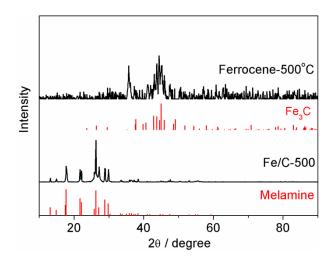
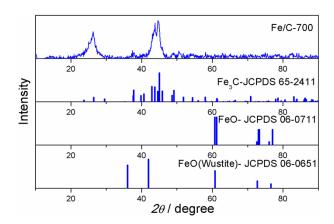


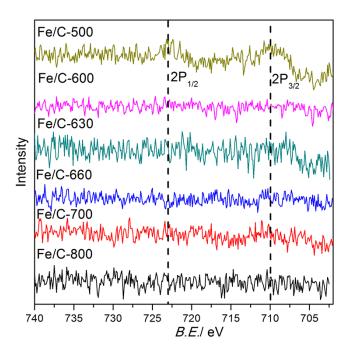
Fig. S2b HRTEM image of a Fe<sub>3</sub>C nanoparticle in Fe/C-600



**Fig. S3** XRD patterns of Fe/C-500 and the product obtained by using ferrocene as the precursor pyrolyzed at 500°C.



**Fig. S4** XRD patterns of Fe/C-700 and the standard XRD patterns assigned for Fe<sub>3</sub>C and two types of iron oxide.



**Fig. S5** High resolution XPS spectra of Fe-2p for Fe/C-500, Fe/C-600, Fe/C-630, Fe/C-660, Fe/C-700 and Fe/C-800.

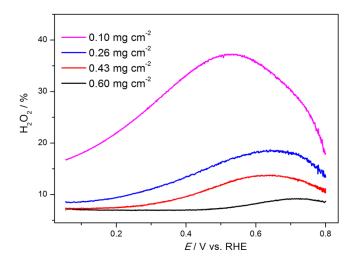


Fig. S6 Peroxide yields of Fe/C-700 (at different loadings) for ORR in 0.1M HClO<sub>4</sub>.

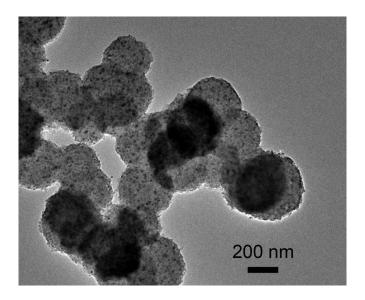
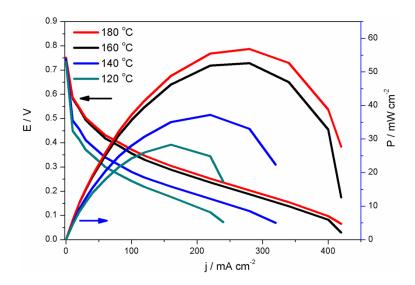
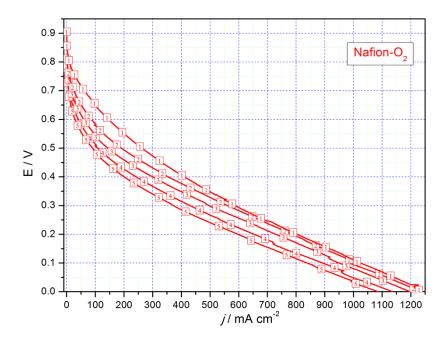


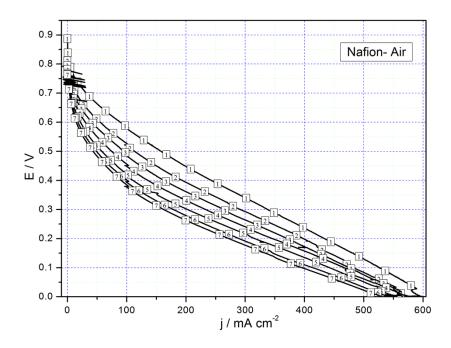
Fig. S7 Catalyst spheres of Fe/C-800 after the AST test in  $O_2$ .



**Fig. S8** Polarization and power density curves of the PBI-2 H<sub>2</sub>-O<sub>2</sub> fuel cell different working temperatures under ambient pressure. The catalyst loading is 3.95 mg cm<sup>-2</sup>. See Experimental Section for other operation conditions.



**Fig. S9** Plolarization curves obtained throughout stability test of Nafion-O<sub>2</sub> (shown in Figure 9) at various times, i.e. 0 h (1), 2.0 h (2), 7.7 h (3), 26.4 h (4), and 50.0 h (5). The catalyst loading in the cathode is 3.95 mg cm<sup>-2</sup>. The fuel cell temperature is 80 °C. See Experimental Section for other operation conditions.



**Fig. S10** Plolarization curves obtained throughout stability test of Nafion- Air (shown in Figure 9) at various times, i.e. 0 h(1), 2.0 h (2), 7.7 h (3), 26.4 h (4), 50.0 h (5), 75.6 h (6) and 100.0 h (7). The catalyst loading in the cathode is 4.08 mg cm<sup>-2</sup>. The fuel cell temperature is 80 °C. See Experimental Section for other operation conditions.