Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting materials

Synchrotron radiation *in-situ* X-ray absorption fine structure and *in-situ* X-ray diffraction analysis of a high-performance cobalt catalyst towards oxygen reduction reaction

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The apparent exchange current density is one of the most important parameter to reflect the activity of a catalyst. The apparent exchange current density could be obtained by the analysis of electrochemical impedance spectra (ESI) collected on the DBFCs at open circuit condition. We carried out the EIS test on a Gamry interface 1000 analyzer in a three-electrode system at room temperature. The AC frequency was varied from 10 mHz to 10 kHz with an amplitude of 5 mV for EIS test.

Fig. S1 shows the ESI of Co-PPy-BP cathode collected on the DBFCs at open circuit condition in a three-electrode system. The diameter of the semicircle at the low frequency (R^{OCV}) is attributed to the electrochemical reaction resistance for the ORR at open circuit condition. The equivalent circuit proposed by Zhang *et al*. is used to simulate the Nyquist plots recorded on the DBFC and then the value of R^{OCV} is obtained [R1]. Based on the calculated R^{OCV} and Eq. (1), the apparent exchange current density ($i^{\mathrm{o}}_{\mathrm{O_2}}$) for the ORR at the DBFC using Co-PPy-BP cathode can be calculated [1].

$$R^{\mathrm{OCV}} = \frac{RT}{n_{\alpha\mathrm{O}} F i^{\mathrm{o}}_{\mathrm{O_2}}} \qquad (1)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), $n_{\alpha\mathrm{O}}$ is the electron transfer numbers of the catalyst towards ORR.

The values of $n_{\alpha\mathrm{O}}$ of Co-PPy-BP cathode is 3.72, which are calculated by Koutecky-Levich plots according to the RDE voltammograms (Fig. 2c). Based on Eq. (1), the apparent exchange current density is calculated to be 3.06×10^{-4} A cm^{-2}. The apparent exchange current density for the Co-PPy-BP cathode catalyzed ORR is higher than that obtained with commercial Pt/C cathode in PEMFC (1.22×10^{-4} A cm^{-2}) [1]. The better ORR kinetics of the Co-PPy-BP cathode in DBFC is attributed to that the electrochemical reaction of ORR in alkaline media is much faster than that in acidic media.

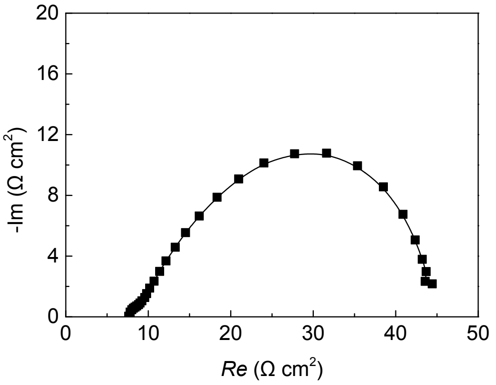

Fig. S1. Electrochemical impedance spectra for the Co-PPY-BP cathode in DBFC at room temperature.

The TEM results of the Co cathode after stability test for 70 h are shown in the following (Fig. S2). Besides the Co nanoparticles, some needle-like and plate-like Co compounds are observed as shown in Fig. S2a. The lattice distance of the needle-like compound is ~0.44 nm, which is consistent with the (003) plane interval of CoOOH (Fig. S2b). The corresponding electron diffraction pattern (Fig. S2c) is weaker and more dispersive than the pattern shown in Fig. 1d. All of the results agree with your deduction that the oxidization reaction occurs at the whole of Co particle and there is a structural decomposition.

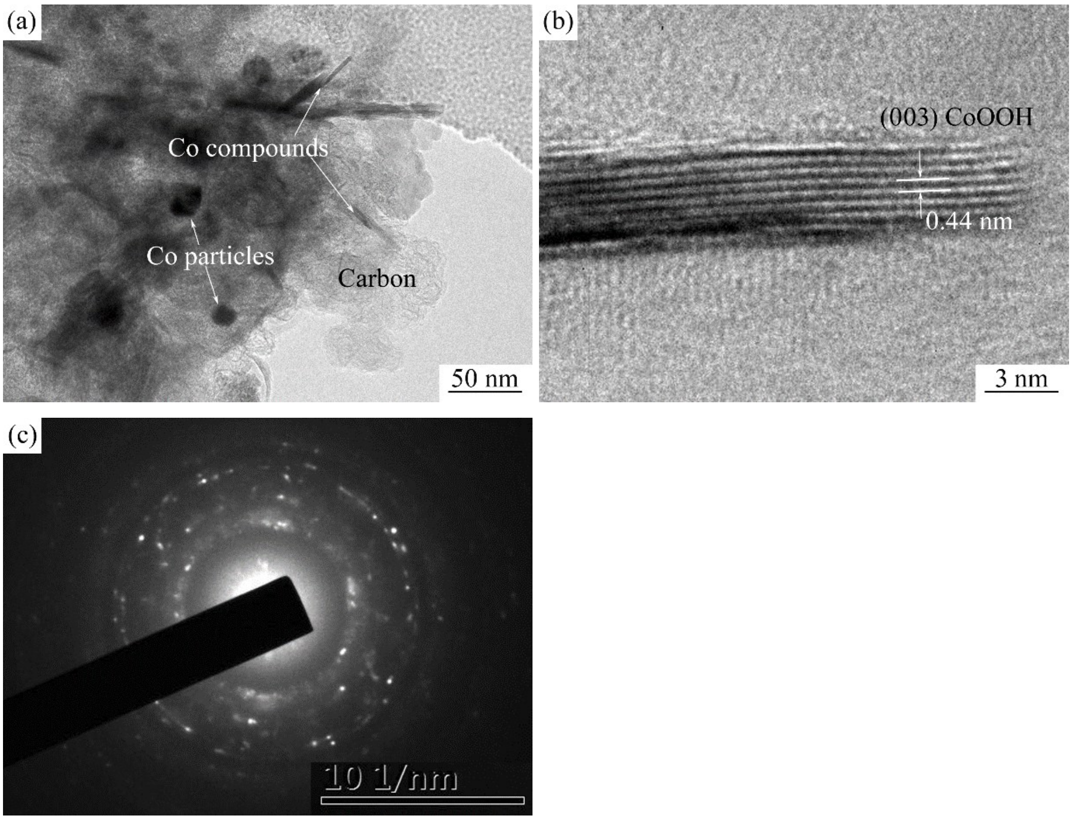

Fig. S2. (a) Bright-field TEM image, (b) high-resolution TEM image and (c) corresponding selected area electron diffraction patterns of the Co cathode after stability test for 70 h.

The change of the cell voltage at various set currents during XAFS test is given in Fig. S3. The cell voltage keeps rather stable during each 20 min for XAFS test. However, it should be admired that 20 min is too short to evaluate the stability of a catalyst.

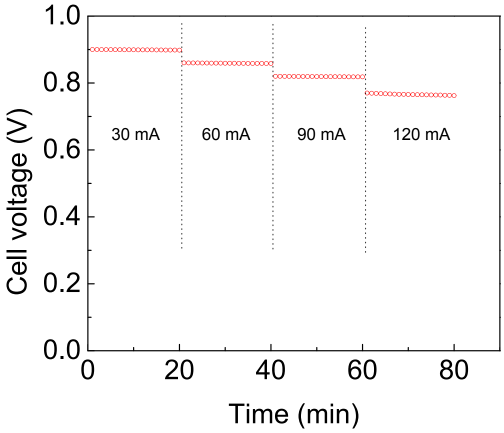

Fig. S3. The change of the cell voltage at various set currents during XAFS test.

References:

[1] Zhang J L, Tang Y H, Song C J, Zhang J J, Wang H J, PEM fuel cell open circuit voltage (OCV) in the temperature range of 23 °C to 120 °C[J]. Journal of Power Sources, 2006, 163(1): 532-537.

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