

Tuning the Oxidation State of Manganese Oxide Nanoparticles on Oxygen- and Nitrogen-Functionalized Carbon Nanotubes for the Electrocatalytic Oxygen Evolution Reaction

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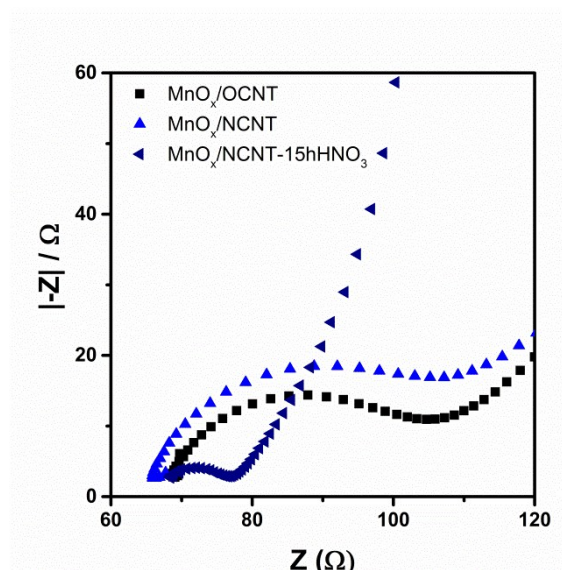


Figure S1. Electrochemical impedance spectra (EIS) of various MnO_x/OCNT and MnO_x/NCNT samples recorded in KOH (0.1 M) at zero current, and at using ac perturbation of 10^{-4} A.

The results obtained from the Nyquist plots in Fig. S1 show that the charge transfer resistance was generally lower for the NCNT supported catalysts (MnO_x/OCNT : $32.6 \Omega \text{ cm}^2$, MnO_x/NCNT : $29.2 \Omega \text{ cm}^2$, $\text{MnO}_x/\text{NCNT-15hHNO}_3$: $7.8 \Omega \text{ cm}^2$), implying that interfacial charge transfer and hence the kinetics of the OER was more favorable for the NCNT supported catalysts. The different thermal treatment conditions thus clearly affect the electronic properties of the CNTs, and ultimately their electrocatalytic properties.

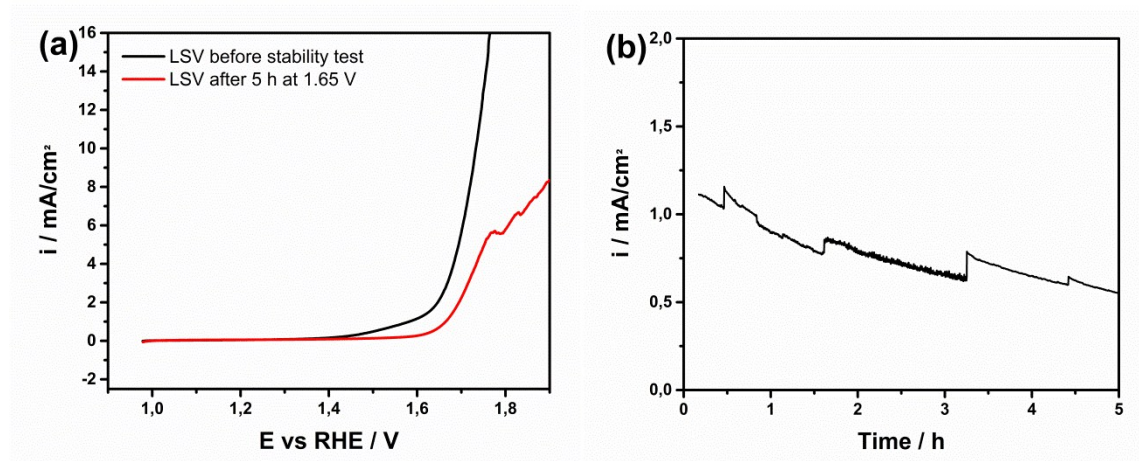


Figure S2. Linear sweep voltammograms of $\text{MnO}_x/\text{NCNT-15hHNO}_3$ recorded in KOH (0.1 M) at 5 mV/s and 1600 rpm, before and after 5 h of stability testing (a), and (b) chronoamperometry showing the current response of the sample in the course of 5 h of continuous polarization at 1.65 V vs RHE.

Figure S2 shows several long-term stability tests, which involved a sequence of, firstly, 100 CVs cycles at 100 mV s^{-1} with electrode rotation at 1600 rpm in 0.1 M KOH between 1.0 V and 1.5 V for conditioning of the electrode, followed by a repeated sequence of galvanostatic EIS at zero current, LSV at 5 mV s^{-1} and 1600 rpm, and chronopotentiometry at 1.65 V versus

RHE for 5 h. Typical LSVs showing the initial performance of the catalyst, and its performance after 5 h of polarization at 1.65 V for 5h, and the corresponding chronoamperometric response. In the course of the stability measurements, huge gas bubbles were seen to gradually build up at the electrode surface accompanied by decline of the measurement current. As can be seen in the figure above, the current increased whenever the gas bubbles detached from the electrode surface, then decreased again with subsequent bubble accumulation. In the most severe case, the entire film completely detached from the electrode leading to a drastic decline of the activity. Thus, a better technique for immobilization of the catalysts films needs to be developed in order to investigate the chemical stability of the catalysts under the aggressive oxygen evolution conditions.

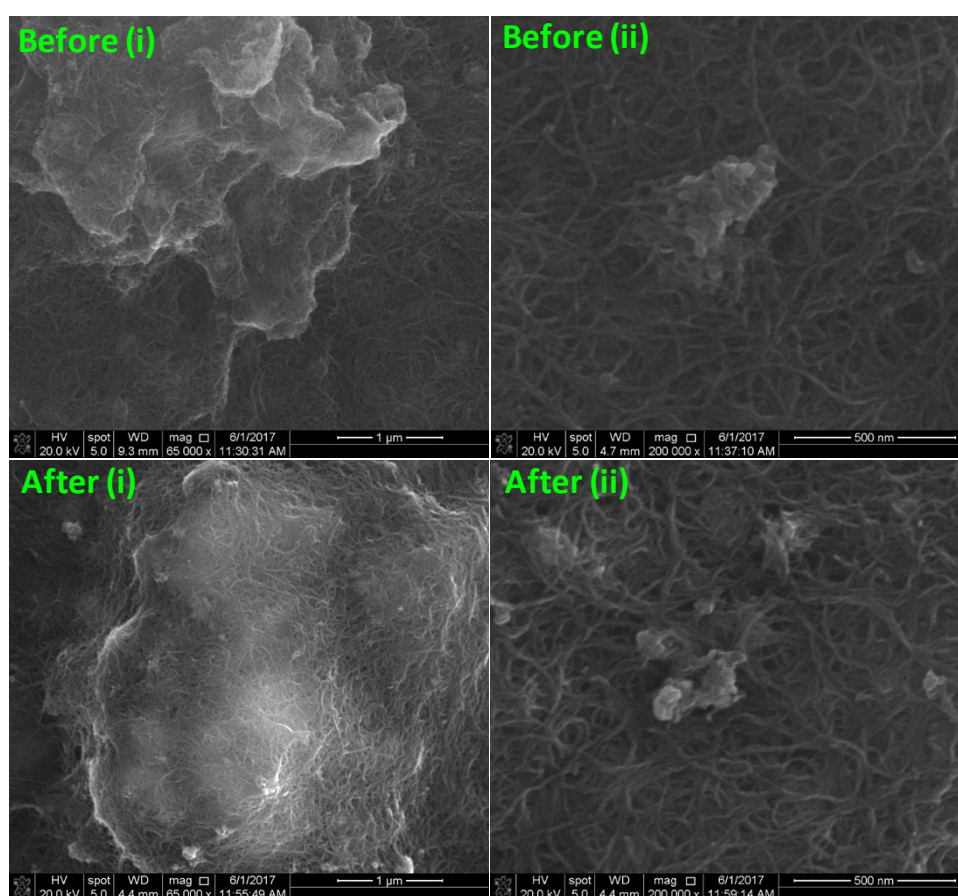


Figure S3. SEM images of MnOx/NCNT-15hHNO₃ at different magnification scales before (i), and after (ii) stability testing.

No obvious changes in the morphology of the catalyst were observed after reaction.