Efficient electrocatalytic oxygen reduction over self-supported polyaniline-based non-precious metal catalyst

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A new approach to prepare self-supported non-precious metal catalysts (NPMCs) for oxygen reduction reaction (ORR) was proposed. With this approach, nanoworm-shaped NPMCs for ORR were synthesized with polyaniline nanofibers as both nitrogen as well as carbon precursors. The high onset potential (0.905V vs. RHE) and the near four-electron transfer mechanism for ORR of prepared catalysts testified the reliability of this approach in formation of active sites with high intrinsic activity. A significant enhancement in the intrinsic activity and onset potential for the ORR is observed when the Fe content in the precursor is increased from 0 to 3.0 wt.%, suggesting the possible existence of two types of active sites formed in the absence and presence of the ferrous salt in the precursor.

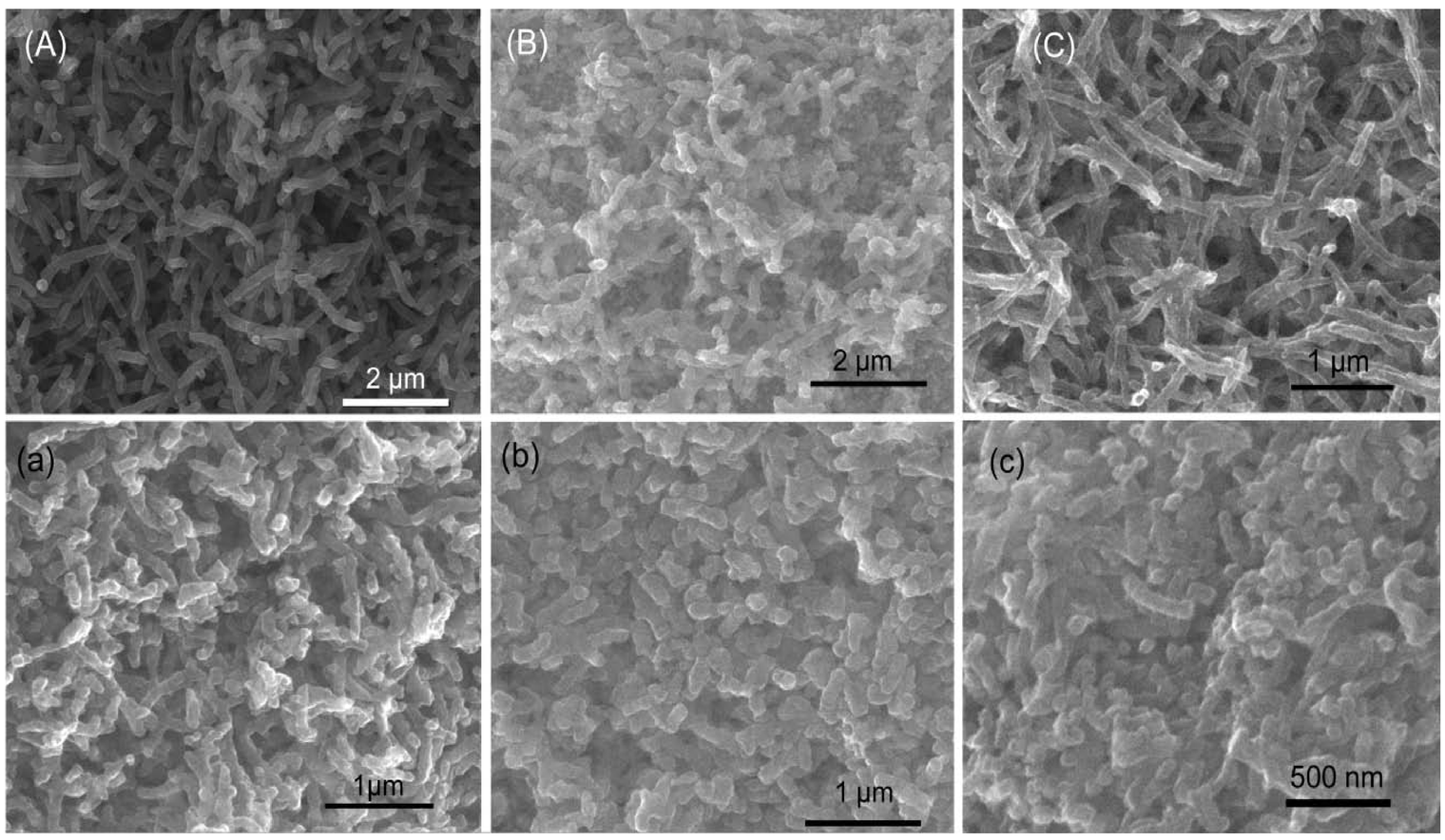

Fig. 1 SEM images of PANI nanofibers: (A) PANI-1, (B) PANI-2, (C) PANI-3 and the corresponding final catalysts with initial Fe content of 1.0 wt.%: (a) 1.0Fe-PANI-1-L, (b) 1.0Fe-PANI-2-L, (c) 1.0Fe-PANI-3-L.

ORR activity: The onset potential of 3.0Fe-PANI-L for the ORR was found to at 0.905V *vs*. RHE, which was about 0.1 V lower than that of the commercial Pt/C catalyst (1.05V *vs*. RHE). This value was close to that of the best PANI-based catalysts reported in literatures [1].

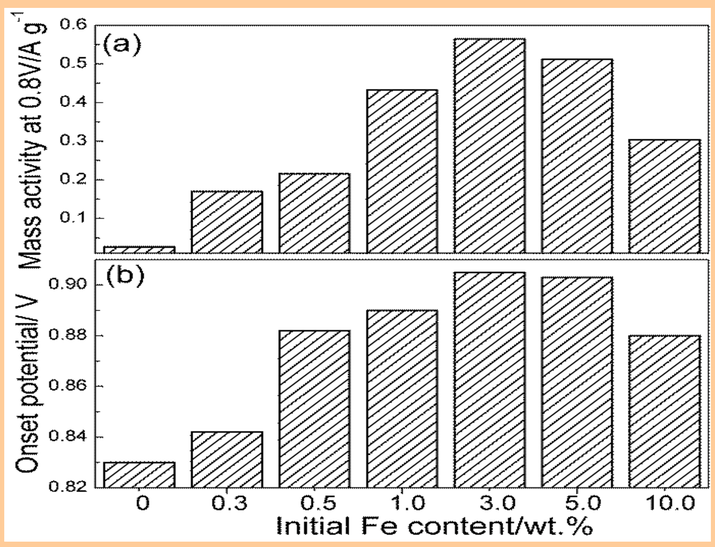

Fig. 3 (a) Kinetic current densities at 0.8 V derived from Tafel graphs and (b) onset ORR potentials for the catalysts depicted in Fig. 2.

Catalyst morphology: The nanofiber structures of the PANI precursor were found to be primarily preserved during the synthesis and the following treatments of NPMCs. This interesting phenomenon provides an approach to preparation of the self-supported NPMCs by employing nano-structured precursors.

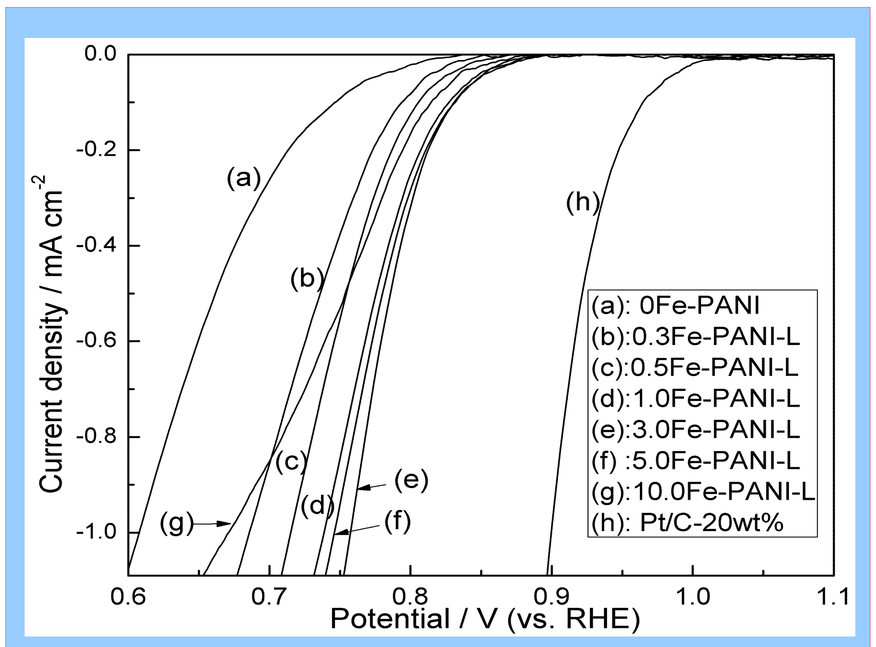

Fig. 2 ORR polarization curves for different catalysts in the low over-potential region: (a) 0Fe-PANI, (b) 0.3Fe-PANI-L, (c) 0.5Fe-PANI-L, (d) 1.0Fe-PANI-L, (e) 3.0Fe-PANI-L, (f) 5.0Fe-PANI-L (g) 10.0Fe-PANI-L and (h) Pt/C in O_2 saturated solution of pH 1 at 1000 rpm. Scan rate: 10 mV s^{-1}. Electrolyte: H_2SO_4 for NPMCs and $HClO_4$ for Pt/C. Catalyst loading: 0.6 mg cm^{-2} for NPMCs and 40 μg_{Pt} cm^{-2} for Pt/C.

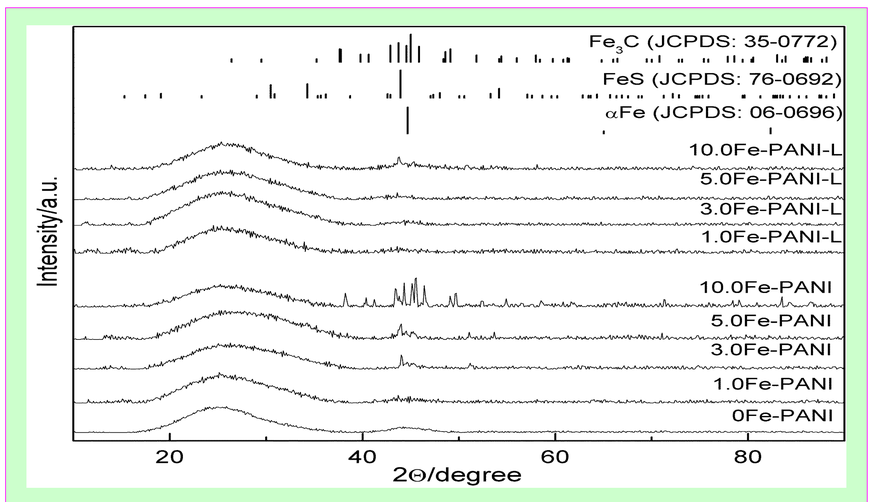

Fig. 4 XRD patterns for 0Fe-PANI, 1.0Fe-PANI, 3.0Fe-PANI, 5.0Fe-PANI, 10.0Fe-PANI and 1.0Fe-PANI-L, 3.0Fe-PANI-L, 5.0Fe-PANI-L, 10.0Fe-PANI-L.

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References

[1] G. Wu, C.M. Johnston, N.H. Mack, K. Artyushkova, M. Ferrandon, M. Nelson, J.S. Lezama-Pacheco, S.D. Conradson, K.L. More, D.J. Myers, P. Zelenay, J. Mater. Chem., 21 (2011) 11392-11405.