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Role of iron in the reduction of H_2O_2 intermediate during the oxygen reduction reaction on iron-containing polyimide-based electrocatalysts

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Experimental details

The precursor for Fe-N-C catalyst was synthesized from the pyromellitic acid dianhydride and 4,4’-oxydianiline in the presence of tris(acetylacetonato) iron (III) (Fe(acac)$_3$). For fuel cell catalysts it is necessary to synthesis the nanoparticle sized polymers (low molecular weight polymers). In order to synthesize the smaller nano-sized polymer particles, polymerization has been carried out fairly a low concentration with high monomeric concentration [Y. Nabae, Y. Kuang, M. Chokai, T. Ichihara, A. Isoda, T. Hayakawa and T. Aoki, *J. Mater. Chem. A*, 2014, **2**, 11561-11564]. The precursor was subjected to multi-step pyrolysis and finally the carbonized product is used for the study of the ORR in acidic medium. To retain the maximum nitrogen content in the catalysts after the pyrolysis, the multi-step pyrolysis was adopted. The pyrolyzed product was acid-washed in between the pyrolysis steps to remove the excess iron which is believed to reduce the nitrogen content. The Fe containing polyimide precursor was heated at 600 °C for 5 hrs under nitrogen atmosphere and again heated to 800 °C and 1000 °C for each 1 hr in ammonia (50% balanced by nitrogen) atmosphere. The pyrolysis yields at 600, 800 and 1000 °C were 50, 54 and 34%, respectively. The product was washed with conc. HCl after each of the heat treatments at 600 and 800 °C and the final product is designated as Fe/PI. Fe-free PI catalyst was also prepared by pyrolyzing the similar precursor but without Fe. The different protocol was used for the Fe-free precursor since the Fe-free precursors did not yield any carbonized product. To obtain a reasonable amount of Fe-free PI catalyst, the Fe-free precursor was heated at 900 °C for 5 hrs under nitrogen atmosphere (yield: 46%) and again heated to 800 °C for 1 hr in ammonia (50% balanced by nitrogen; yield: 80%). The HCl wash was not applied for the Fe-free PI catalyst. All the heat treatments were conducted by gradual heating (typical ramping rate: 10 °C min^{-1}) with abundant gas flows (over 1 L min^{-1}).

Rotating disk electrode voltammograms

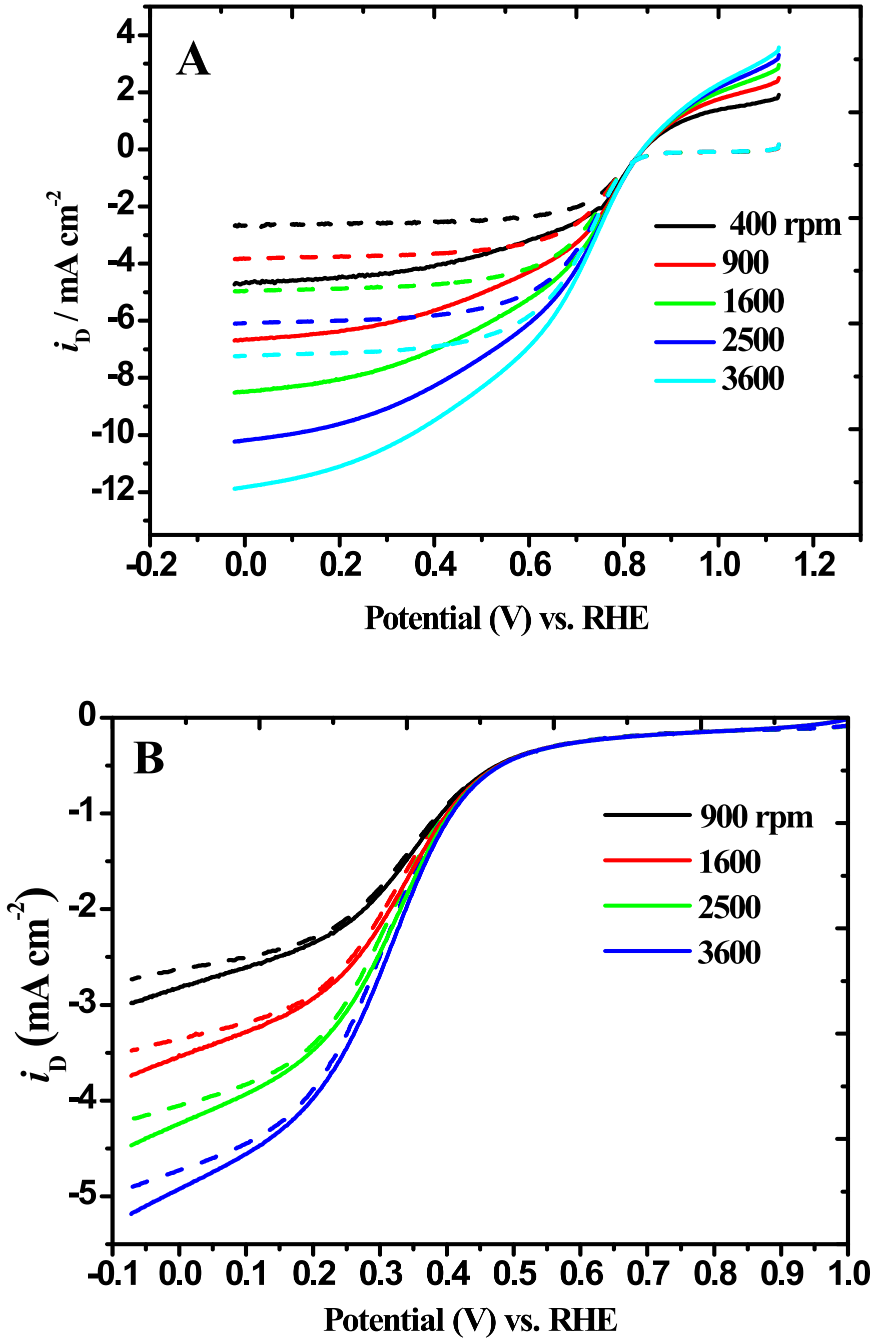

Figure S1. Steady-state voltammograms for the reduction of 2.0 mM H_2O_2 (solid lines) on the (A) Fe/PI and (B) Fe-free PI coated GC electrode in O_2-saturated 0.5 M H_2SO_4 solution at 5 mVs^{-1} scan rate and various rotational speeds. The dotted lines indicate the voltammograms for the ORR in O_2-saturated 0.5 M H_2SO_4 solution.