

Evaluation of IrO₂ Activity as an Electrocatalyst for Oxygen Evolution Reaction by Heteroatom doped Reduced Graphene Oxide

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Electrochemical water splitting in polymer electrolyte water electrolyzers is an excellent way to produce hydrogen as an energy source for applications such as aerospace engineering, semiconductor manufacturing and energy devices, etc. For generation of hydrogen at a specific rate, under ideal conditions, 1.23 V must be supplied to the electrochemical system. In practice, water splitting is limited by the slow reaction kinetics on the electrodes, especially, reaction at the anode, i.e. oxygen evolution reaction (OER)¹. OER is a complex reaction with high over-potential and slow kinetics which requires precious metal catalysts such as iridium and ruthenium oxides (IrO₂, RuO₂) to proceed efficiently with reducing reaction overpotential. However, their high cost and low natural abundance limit their extensive commercialization. The most plausible solution can be the reduction of metal loading amount in catalysts by increasing active surface area and/or modifying the electronic structure of catalysts to improve specific activity. Modification of the electronic structure can be achieved by heteroatom-doping of the carbon support and higher surface area can be obtained by designing nanoparticles (nps) with smaller size. In the current research, we synthesized IrO₂ nps catalyst using heteroatom-doped reduced graphene oxide (rGO) as the carbon support. Along with alteration of the electronic structure of the IrO₂ nps, heteroatom-doping of graphene² also promotes ion diffusion at the electrode-electrolyte interface which improves the overall performance of the catalyst.

Graphene oxide (GO) was prepared from synthetic graphite (Sigma Aldrich) by modified Hummer's method. Boric anhydride (BA) was used as the boron source for doping. Pyrolysis of BA and GO was carried out at 1000 °C for 60 min in N₂ atmosphere. The pyrolysed sample was washed with water and ethanol to yield boron doped rGO (B-rGO). In the second step, IrO₂ nps were decorated onto B-rGO by hydrothermal synthesis at 150 °C for 4 h using H₂IrCl₆ as the precursor. The synthesized materials were characterized for its chemical composition, morphology and electrocatalytic activity using various analytical techniques such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

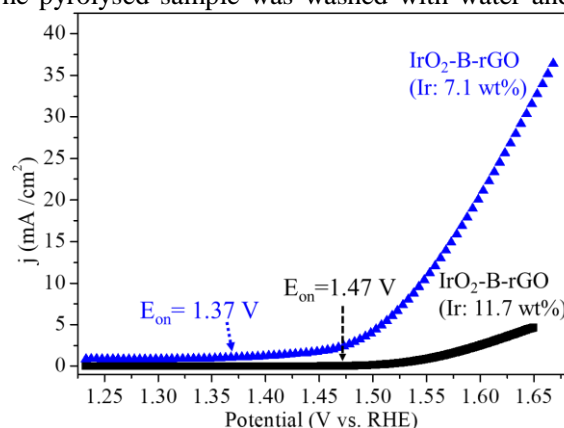


Fig. 1. OER electrocatalytic activity on IrO₂-B-rGO and IrO₂-rGO in 0.5 M H₂SO₄.

XPS analysis of the synthesized catalyst revealed the presence of all constituent elements at their respective binding energies. Deconvolution of C1s peak indicated the extent of reduction of GO and that of B1s peak displayed the types of constituent B in B-rGO. Ir 4f peaks for the synthesized catalysts were shifted (~0.5 eV) to lower binding energies than IrO₂ powder exhibiting the change in electronic states of Ir due to heteroatom doping. Further, the elemental composition and homogeneity was confirmed by EDX analysis. TEM analysis confirmed the uniform dispersion of IrO₂ over wrinkled B-rGO sheets with an average particle diameter of 1.5 nm. Electrochemical activity towards OER was studied via CV and LSV methods with rotating disk electrode (RDE) system in 0.5 M H₂SO₄ solution. Electrochemical analysis showed that the onset potential (E_{on}) was 1.37 V vs RHE for B doped catalyst, which was ~100 mV less than that of IrO₂-rGO (E_{on} =1.47 V) (Fig. 1). Higher current density was obtained for IrO₂-B-rGO (Ir: 7.1 wt%) as compared to IrO₂-rGO with high Ir content (~12 wt% Ir). Increase in current density for B-doped catalyst is attributed to electron transfer between heteroatom-doped support to IrO₂ which alters the electronic states for Ir and provides additional active centres for catalysis.

- 1) C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo *J. Am. Chem. Soc.* **135**, 16977–16987 (2013).
- 2) J. Zhang and L. Dai, *ACS Catal.* **5**, 7244–7253 (2015).