

Can Graphene be an electrode support for Pt in formic acid electrooxidation?

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The electrode supports play an important role in anchoring the noble metal catalysts such as Pt and Pd in a fuel cell. The main roles of electrode support materials are catalyst dispersion, charge transport, and stabilization of the catalyst particles. Carbon functions as an excellent support with all the aforementioned properties. Different morphology with high surface area and functional groups on the carbon materials can be utilized as the electrode support for anchoring precious metals. Mainly carbon in the form of carbon nanotubes, carbon nanofibers, and fullerenes has been used as an electrode support. They have shown improved electro oxidation of fuels such as methanol and formic acids as compared to the conventional commercial support Vulcan –XC-72. This is attributed to the inherent properties of the carbon nanostructures, which appears to favor better catalyst dispersion, and formation of smaller, more active catalyst sites.

Recently graphene has been explored for its exceptional electronic properties for different applications like, energy storage device like ultra supercapacitor, photovoltaic and in electronics [1]. The application of graphene as an electrode support is yet to be examined. In this presentation, we have compared the activity of graphene with commercial 20 wt% Pt-carbon (HiSpec 3000) catalyst for formic oxide electro oxidation. Direct formic acid fuel cells (DFAFCs) have attracted much attention since they demonstrate several advantages over direct methanol fuel cell (DMFC) [2, 3]. Although various metals such as Pt, Pd, Rh and a combination of two metals have been examined over Vulcan carbon for formic acid oxidation, their activity over other engineered carbon such as CNT, graphene is yet to be explored.

Graphene can be prepared from inexpensive natural graphite through series of chemical transformations. In this presentation we have followed different synthetic methodology to reduce graphite oxide prepared from graphite by Hummer process [4]. A comparison of reduction process of graphitic oxide has been considered. The reduction has been carried out by refluxing at 100 °C for 24h with hydrazine [5]. Where as, we have adopted ethylenediamine as the reducing agent through ultrasonification process. Overall, we have developed and demonstrated a simple method for the reduction of graphite oxide through ultrasonification process.

The electrodes for the electrochemical measurements were fabricated by dispersing 10 mg of carbon support in 200 μ l of deionized water and 20 μ l of 5 wt% Nafion[®] solution. A known amount of the suspension was deposited over a glassy carbon electrode (GC). The platinum nanoparticles were electrochemically deposited from a deaerated 3 mM solution of chloroplatinic acid (Alfa Aesar, purity 99.99%) in 0.5 M H₂SO₄. The deposition was carried out by cycling 20 times between the potentials of -0.25 V and 1V at a scan rate of 10 mV/s with respect to Ag/AgCl. The electrochemical active surface area (EAS) of the

electrodes was estimated using carbon monoxide (CO) stripping experiments. Formic acid electrooxidation measurements were performed in a 0.5 M HCOOH + 0.5 M H₂SO₄ electrolyte. The stability of the electrodes was evaluated from the current–time plot.

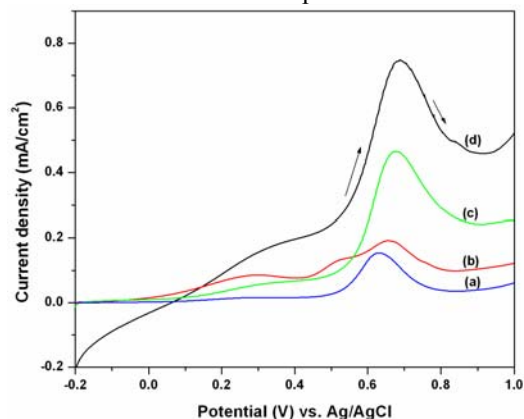


Figure 1 The forward scans measuring HCOOH electrooxidation over (a) Pt/ GC-Vulcan XC-72, (b) GC-HiSpec 3000, (c) Pt/GC-Graphene, (d) Pt/GC-GUE (Arrow indicates the scan direction) (The scan shown in figure is after 5 cycles).

Pt over various supports	CO oxidation peak potential: mV vs. Ag/AgCl	Surface area from CO oxidation: cm ²	Formic acid onset oxidation: mV vs. Ag/AgCl	Forward peak current density: mA cm ⁻²
Pt/GC-Vulcan XC-72	500	9.48	498	0.15
Hi-Spec 3000	626	35.13	546	0.18
Pt/GC-Graphene	460	3.83	522	0.46
Pt/GC-GUE	479	0.2	494	0.75

Table 1 Electrochemical parameters for CO stripping and formic acid oxidation over the different electrodes.

The Pt deposits over graphene demonstrate an enhancement in the formic acid electrooxidation over commercial catalysts. The data from Table 1 and Figure 1 clearly shows the advantage using graphene as the support for anchoring Pt. An enhanced electro oxidation of formic acid as well as a shift in the onset of formic acid oxidation potential has been noted. The activity of graphene is of 4 times higher than the commercial catalyst. Graphene can be potential electrode support for effective anchoring of other precious metal particle(s) in fuel cell electrocatalyst development.

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