Supplementary Materials: An Oxygen Reduction Study of Graphene-Based Nanomaterials of Different Origin

Jaana Lilloja, Elo Kibena-Põldsepp, Maido Merisalu, Protima Rauwel, Leonard Matisen, Ahti Niilisk, Eduardo S.F. Cardoso, Gilberto Maia, Väino Sammelselg and Kaido Tammeveski

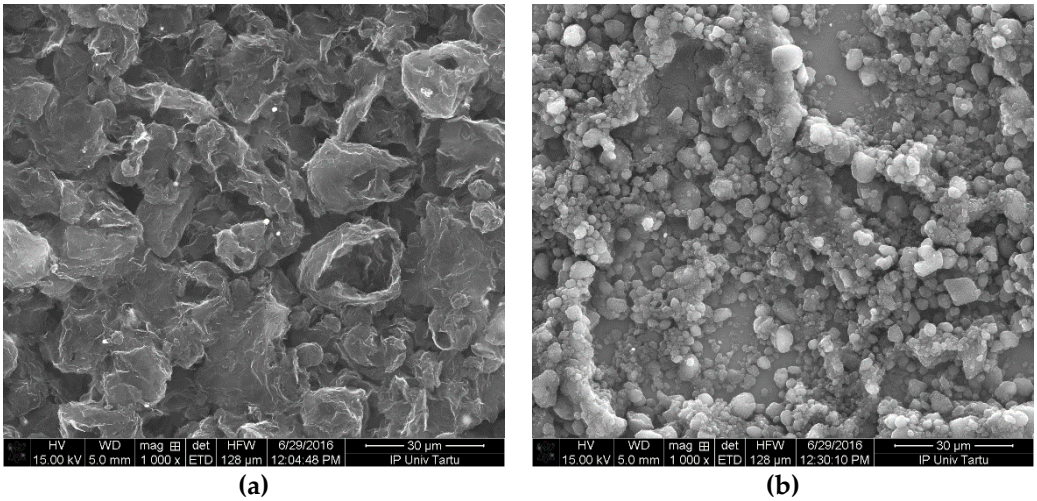
1. Synthesis of Graphene Oxide (GO)

For the synthesis of GO by the modified Hummers' method [1] as reported elsewhere [2], 50 mL of concentrated sulphuric acid and 2 g of natural graphite powder (Graphite Trading Company) were mixed in a 250 mL beaker at room temperature. Then, the mixture was sonicated about 1 h. Thereafter, 2 g of sodium nitrate was added followed by the slow addition of 6 g of potassium permanganate. At the same time the mixture was stirred on a magnetic stirrer. Afterwards, the mixture was heated at 35 °C for 18 h. After 18 h, the beaker was put into an ice bath followed by addition of 80 mL Milli-Q water to the solution. Few minutes later, 20 mL of H_2O_2 (30%) was added. The mixture was washed few times with 10% HCl solution and with Milli-Q water by centrifugation. Finally, the obtained brown solid was dried in vacuum at 75 °C.

2. Synthesis of Reduced Graphene Oxide (rGO)

rGO was synthesised similarly as reported by Lima et al. [3,4]. Briefly, 5 mL homogeneous aqueous dispersion of GO (5% *w*/*w*) was mixed with 5 mL of aqueous hydrazine sulphate solution (21 mg) and 39 μL of ammonium hydroxide solution (25 wt % in water) in a 20 mL glass vial. After being vigorously shaken for a few minutes, the vial was placed in a water bath (~95 °C) for 150 min. rGO was obtained after centrifugation to remove any aggregates remained in the suspension and then washed with 0.5% v/v ammonium hydroxide solution (100 mL). Excess ammonium hydroxide was removed by washing with Milli-Q water until a pH similar to Milli-Q was achieved. rGO was dried under vacuum at room temperature.

3. Scanning Electron Microscopy (SEM) Studies



(a) **(b)**

Figure S1. SEM images of: (**a**) graphene nanopowder (from Graphene Supermarket) and (**b**) graphene nanoplatelet aggregates (from Strem Chemicals).

4. Oxygen Reduction Studies

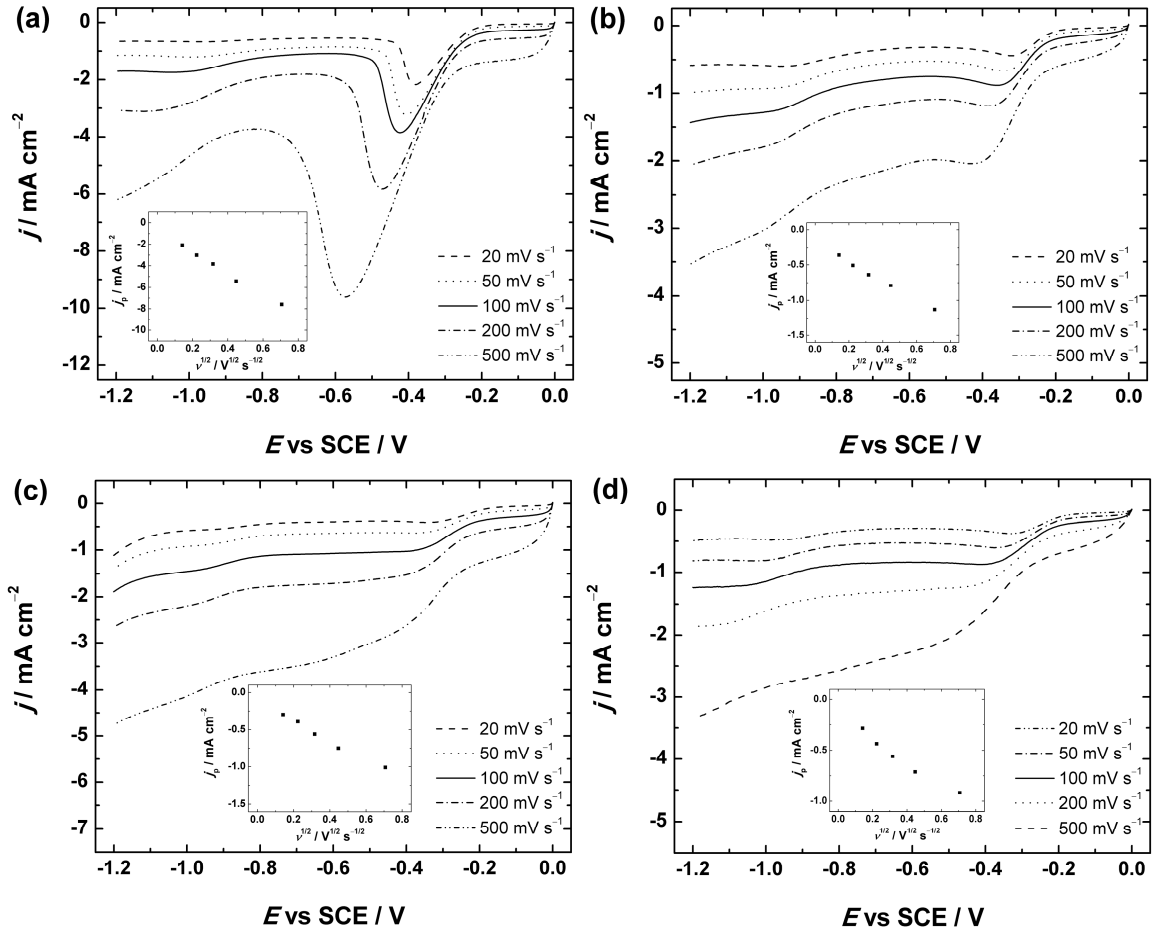


Figure S2. LSV results of O_2 reduction on GC electrodes coated with: (**a**) graphene nanopowder (from Graphene Supermarket); (**b**) graphene nanoplatelet aggregates (from Strem Chemicals); (**c**) graphene oxide and (**d**) reduced graphene oxide. The electrodes were prepared using the catalyst ink suspension in 2-propanol containing OH^- ionomer. The LSVs were registered in O_2-saturated 0.1 M KOH at different scan rates. The insets show the dependence of j_P on $\nu^{1/2}$.

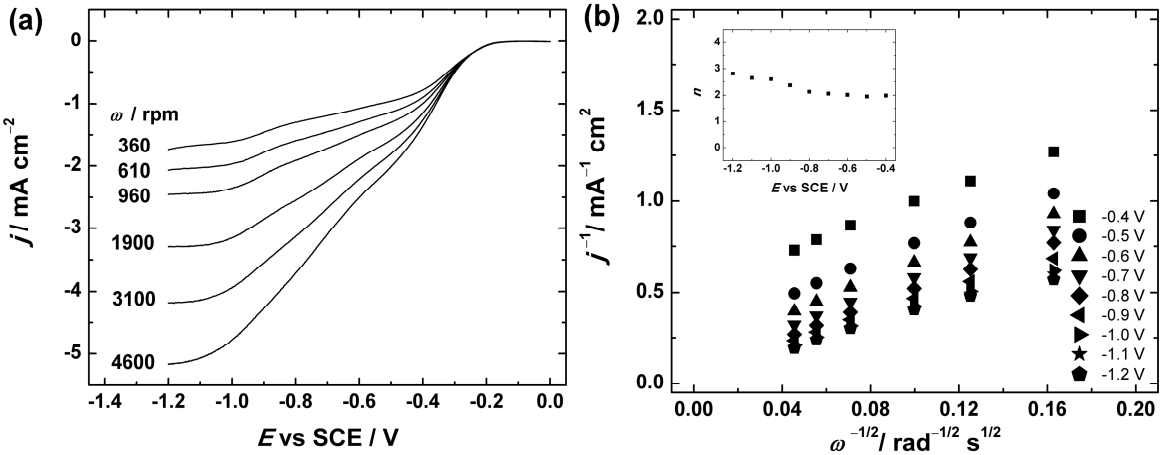


Figure S3. (**a**) RDE voltammetry curves and (**b**) Koutecky-Levich plots for oxygen reduction on GC electrodes coated with graphene oxide in O_2-saturated 0.1 M KOH. ω = 360–4600 rpm, ν = 10 mV·s^{-1}. The inset shows the potential dependence of *n*. The electrode was prepared using the catalyst ink suspension in 2-propanol containing OH^- ionomer.

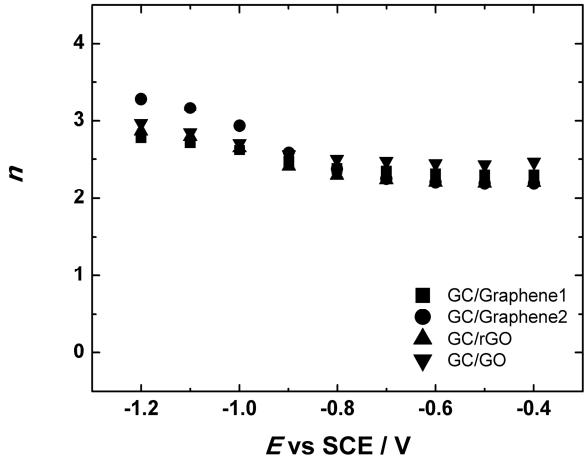


Figure S4. Potential dependence of *n* for GC electrodes modified with graphene nanopowder from Graphene Supermarket (GC/Graphene1), graphene nanoplatelet aggregates from Strem Chemicals (GC/Graphene2), reduced graphene oxide (GC/rGO) and graphene oxide (GC/GO) in O_2-saturated 0.1 M KOH. The electrodes were prepared using the catalyst ink suspension in 2-propanol containing OH^- ionomer. Data derived from Figure 7.

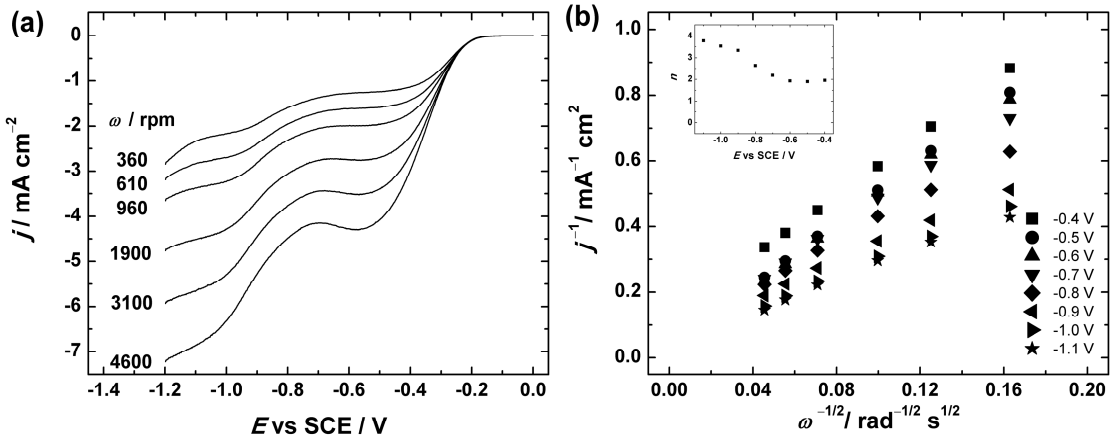


Figure S5. (**a**) RDE voltammetry curves and (**b**) Koutecky-Levich plots for oxygen reduction on GC electrodes coated with graphene oxide in O_2-saturated 0.1 M KOH. ω = 360–4600 rpm, ν = 10 mV·s^{-1}. The inset shows the potential dependence of *n*. The electrode was prepared using the catalyst ink suspension in DMF.

References

1. Hummers, W.S.; Offeman, R.E. Preparation of graphitic oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1339.
2. Vikkisk, M.; Kruusenberg, I.; Joost, U.; Shulga, E.; Kink, I.; Tammeveski, K. Electrocatalytic oxygen reduction on nitrogen-doped graphene in alkaline media. *Appl. Catal. B-Environ.* **2014**, *147*, 369–376.
3. Lima, F.; Fortunato, G.V.; Maia, G. A remarkably simple characterization of glassy carbon-supported films of graphite, graphene oxide, and chemically converted graphene using $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ and O_2 as redox probes. *RSC Adv.* **2013**, *3*, 9550–9560.
4. Lima, F.; Maia, G. Oxidized/reduced graphene nanoribbons facilitate charge transfer to the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ redox couple and towards oxygen reduction. *Nanoscale* **2015**, *7*, 6193–6207.