

Electronic Supplementary Information

**Electrochemical Deposition of Manganese Oxide-Phosphate-Reduced
Graphene Oxide Composite and Electrocatalysis of
Oxygen Evolution Reaction**

Ahamed Irshad and Nookala Munichandraiah*

Department of Inorganic and Physical Chemistry

Indian Institute of Science, Bangalore - 560012, India

*Corresponding author; e-mail: muni@ipc.iisc.ernet.in; Tel: +91-80-2293 3183

S1: Determination of percentage of carbon in the deposit

It was intended to make a correlation plot between the weight % of GO in the deposition bath and amount of carbon in the electrodeposit. For this, several electrodes were made by keeping the concentration of KMnO_4 at 20 mM in 0.1 M phosphate buffer solution, while the weight % of GO in the electrolyte was gradually varied. Depositions were carried out at -1.05 V vs. SCE for 30 min and EDXA was obtained for each samples. The following equations were used to calculate the relative percentage in each case.

$$\text{Percentage of GO in the electrolyte} = \frac{\text{Weight of GO in the electrolyte}}{\text{Total weight of (GO + KMnO}_4\text{)}} \times 100$$

$$\text{Percentage of C in the deposit} = \frac{\text{Weight \% of C in the deposit from EDXA}}{\text{Total weight \% of (C + K + Mn + O + P)}} \times 100$$

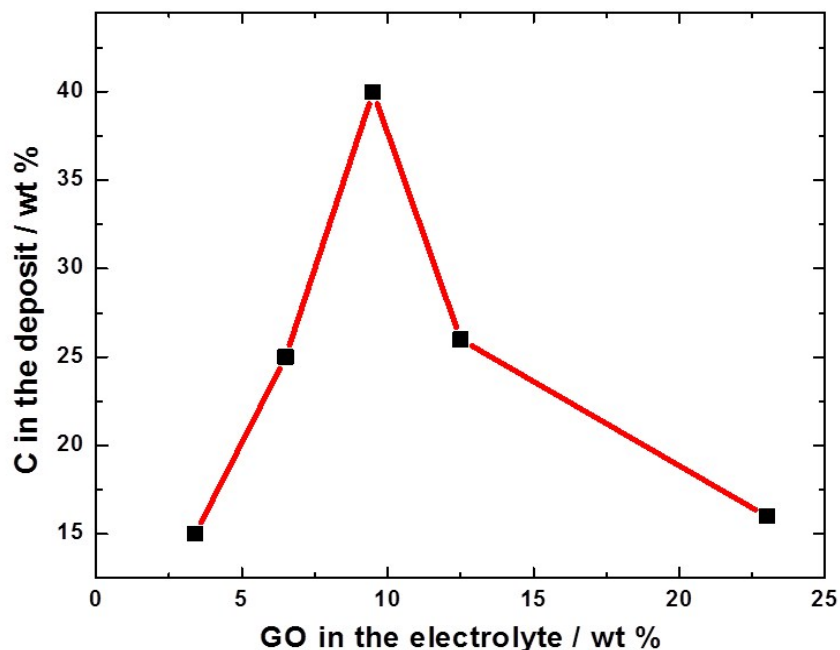


Fig. S1: A plot of % of C in the electrodeposit against weight % of GO in the deposition bath.

S2: Comparison of OER activity

Catalyst	Overpotential at 0.5 mA cm ⁻²	References
MnO_x-Pi-rGO	430 mV	Present work
MnO_x-Pi	560 mV	Present work
MnO₂ (with SDS)	440 mV	ESI-1
MnO₂ (Dau's method)	565 mV	ESI-2
Mn₃(PO₄)₂·3H₂O	680 mV	ESI-3
MnO_x	>700 mV	ESI-4

S3: Faradaic efficiency measurement

The amount of evolved oxygen was quantified using water displacement in an inverted burette. Electrolysis in phosphate buffer solution was carried out at 2.0 V vs. RHE for 1 h in an air-tight glass container consisting of MnOx-Pi-rGO deposited Pt as the working electrode (area = 5 cm²), large Pt foil as the counter electrode and a saturated calomel electrode as the reference. The working electrode was prepared by depositing MnOx-Pi-rGO at -1.05 V vs. SCE for 30 min from 0.1 M neutral phosphate solution containing 20 mM KMnO₄ + 6.5 % GO. The evolved oxygen was collected in a water filled inverted burette. The volume of water displaced in the burette is an estimate for the volume of oxygen generated in the water electrolysis. It was observed that MnOx-Pi produced 71 μmol of oxygen within 1 h of electrolysis and a total charge of 30 C was passed. This corresponds to a Faradic efficiency about 92 %. Similar studies using MnOx-Pi catalyst (ie. without rGO) produced only 53 μmol of oxygen with a Faradic efficiency close to 90 %. Faradic efficiency was calculated using the following equation,

$$\text{The faradaic efficiency} = \frac{n_{\text{O}_2}(\text{experimental})}{n_{\text{O}_2}(\text{theoretical})} \times 100$$

The theoretical number of moles of oxygen evolved was obtained using Faraday's 2nd law of electrolysis according to the following equation,

$$n_{\text{O}_2}(\text{theoretical}) = \frac{Q}{nF} = \frac{i \times t}{nF}$$

where Q is the total charge passed, n is the number of electrons consumed per mole of O₂ (n= 4 for OER), i is the current in amperes, t is the electrolysis time in seconds, and F is the Faraday constant (96485.3 C mol⁻¹).

S4: Stability test

The stability of MnOx-Pi-rGO catalyst was studied by constant potential electrolysis in 0.1 M potassium phosphate buffer solution (pH 7.0). For this, the catalyst was deposited on a Pt substrate at -1.05 V vs. SCE for 30 min from 0.1 M neutral phosphate electrolyte containing 20 mM KMnO₄ + 6.5 % GO. Current trace during electrolysis at 1.95 V vs. RHE is shown in Fig. S4. A current value of 2.7 mA cm⁻² is obtained in the initial stage of electrolysis and it decreases to 1.9 mA cm⁻² after 1 h, indicating a decrease in the current by 30 %.

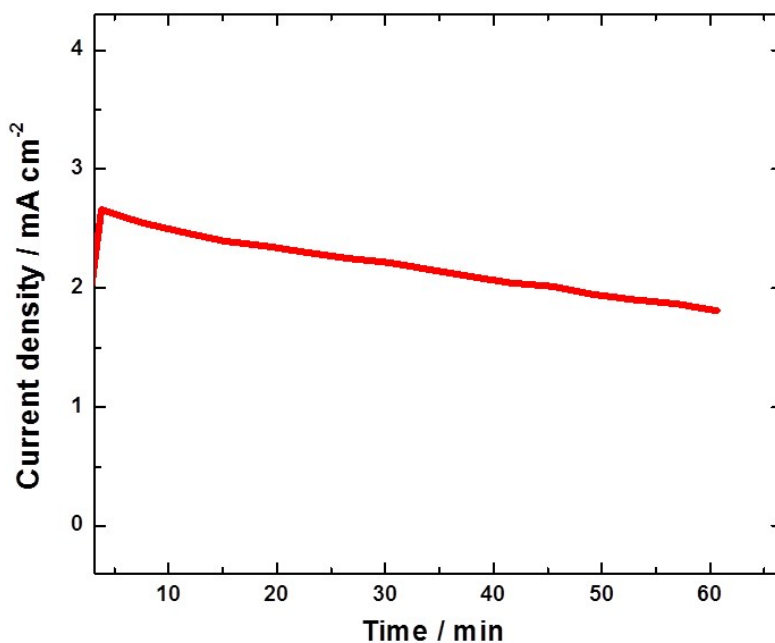


Fig. S4: Amperogram during electrolysis at 1.95 V vs. RHE in 0.1 M phosphate buffer solution (pH 7.0) using MnOx-Pi-rGO catalyst deposited on Pt.

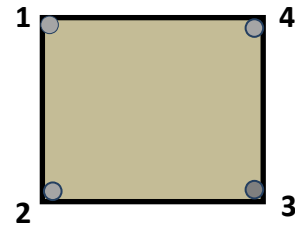
S5: Van der Pauw method for sheet resistance

Electrical conductivity was measured by four-probe Van der Pauw method using Agilent Device Analyzer B1500A. For this, catalysts were deposited on FTO electrodes at -1.3 V vs. SCE for 1 h. A square shaped piece was cut from this and electrical contacts were made at the four corners of the square using silver paste. To make a measurement, a current was passed along one edge of the sample (for instance, I_{21}) and the voltage across the opposite edge (V_{34}) was measured. From these two values, a resistance ($R_{21,34}$) was calculated using Ohm's law. This procedure was repeated in different combinations and then, the sheet resistance (R_S) was obtained by solving the following equation,^{ESI-5}

$$\exp(-\pi R_A / R_S) + \exp(-\pi R_B / R_S) = 1$$

where $R_A = \frac{(R_{21,34} + R_{12,43} + R_{43,12} + R_{34,21})}{4}$, and

$$R_B = \frac{(R_{32,41} + R_{23,14} + R_{14,23} + R_{41,32})}{4}$$



The sheet resistance was found to be $7.5 \Omega / \text{sq}$ for MnOx-Pi-rGO which was almost half that of the MnOx-Pi ($13.6 \Omega / \text{sq}$).

References

[ESI-1]. W. T. Osowiecki, S. W. Sheehan, K. J. Young, A. C. Durrell, B. Q. Mercado and G. W. Brudvig, Surfactant-mediated Electrodeposition of a Water-oxidizing Manganese Oxide, *Dalton Trans.*, 2015, 44, 16873 - 16881.

[ESI-2]. I. Zaharieva, P. Chernev, M. Risch, K. Klingan, M. Kohlhoff, A. Fischer and H. Dau, Electrosynthesis, Functional, and Structural Characterization of a Water-Oxidizing Manganese Oxide, *Energy Environ. Sci.*, 2012, 5, 7081 - 7089.

[ESI-3]. K. Jin, J. Park, J. Lee, K. D. Yang, G. K. Pradhan, U. Sim, D. Jeong, H. L. Jang, S. Park, D. Kim, N. Sung, S. H. Kim, S. Han and K. T. Nam, Hydrated Manganese(II) Phosphate ($\text{Mn}_3(\text{PO}_4)_2 \cdot 3 \text{H}_2\text{O}$) as a Water Oxidation Catalyst, *J. Am. Chem. Soc.*, 2014, 136, 7435 - 7443.

[ESI-4]. M. Huynh, D. K. Bediako and D. G. Nocera, Functionally Stable Manganese Oxide Oxygen Evolution Catalyst in Acid, *J. Am. Chem. Soc.*, 2014, 136, 6002 - 6010

[ESI-5]. L. J. V. Pauw, A Method of Measuring Specific Resistivity and Hall Effect of Discs of Arbitrary Shape, *Philips. Res. Rep.*, 1958, 13, 1 - 9.