Supporting information

WO_3 based solid solution oxide – promising proton exchange membrane fuel cell anode electro-catalyst

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Section S1: The possible reaction scheme for the formation of WO_3 from sodium tungstate dehydrate ($Na_2WO_4.2H_2O$) is given as [1]:

$$Na_2WO_4 + 2HCl \rightarrow H_2WO_4 + 2NaCl$$

$$H_2WO_4 \rightarrow WO_3 + H_2O$$

In the synthesis of WO_3 from $Na_2WO_4.2H_2O$, hydrated tungsten trioxide (H_2WO_4) is obtained as a precipitate and forms pure WO_3 upon further heat treatment. To determine the temperature of heat-treatment of H_2WO_4 and thus, to obtain pure WO_3, thermogravimetric analysis (TGA) was conducted in ultra-high purity Argon (UHP-Ar) atmosphere (Flow rate=40 ml/min) as shown in **Fig. S1**. TGA results show that there is a steady loss in weight upto ~320^{o}C indicative of a transformation of H_2WO_4 to WO_3 (expected weight loss ~7.2%). Hence, heat-treatment of H_2WO_4 was carried out at 350^{o}C for 2 h to obtain pure WO_3.

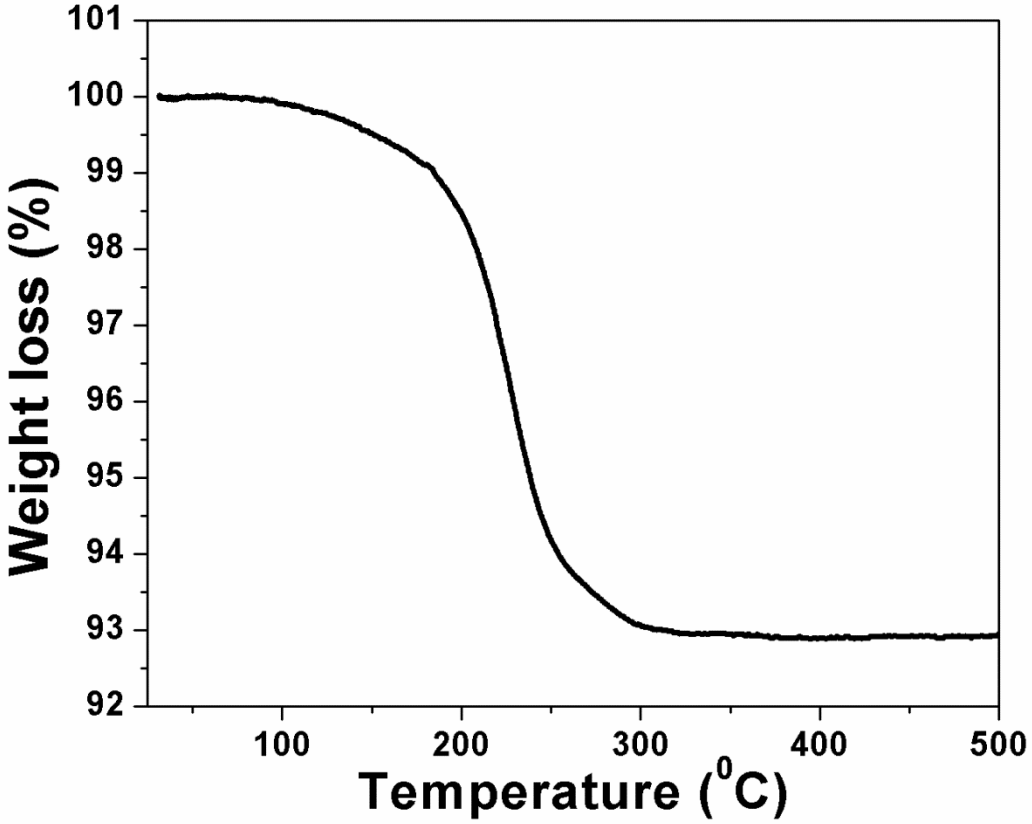

Figure S1: TGA plot of H_2WO_4 powder in UHP-Argon atmosphere showing the weight loss.

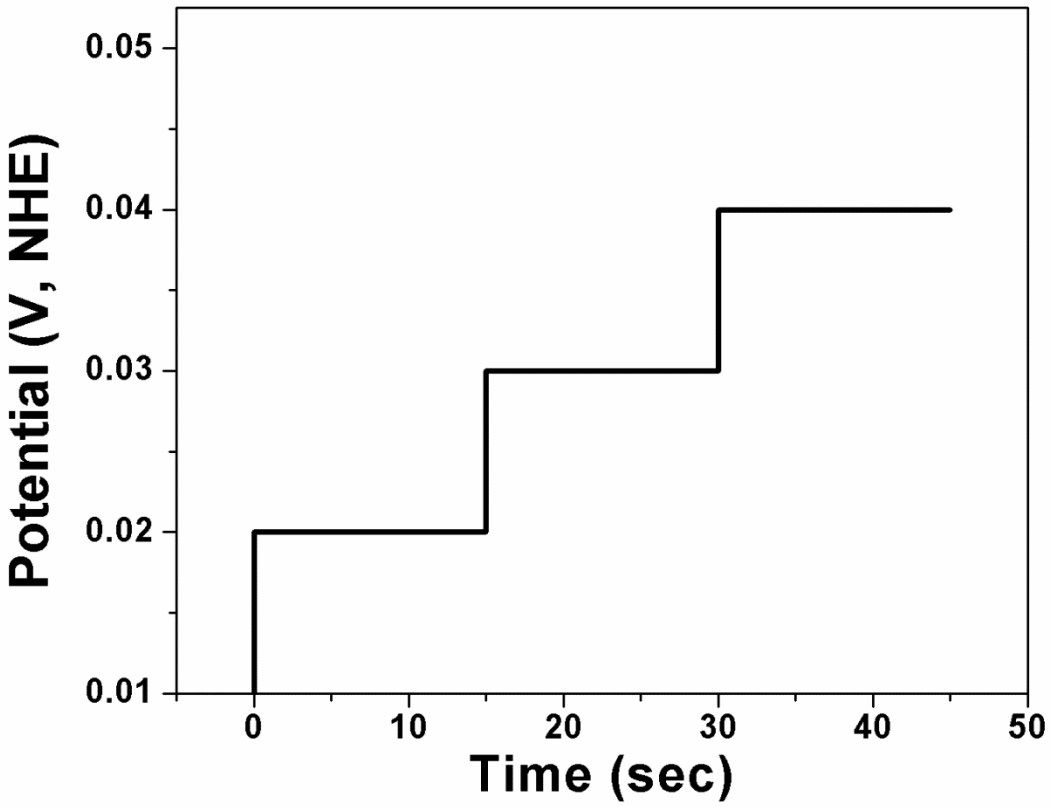

Figure S2: Method of multiple small potential steps used on the RDE to reduce the contribution by charging current and current measurement was performed at the end of each step[2].

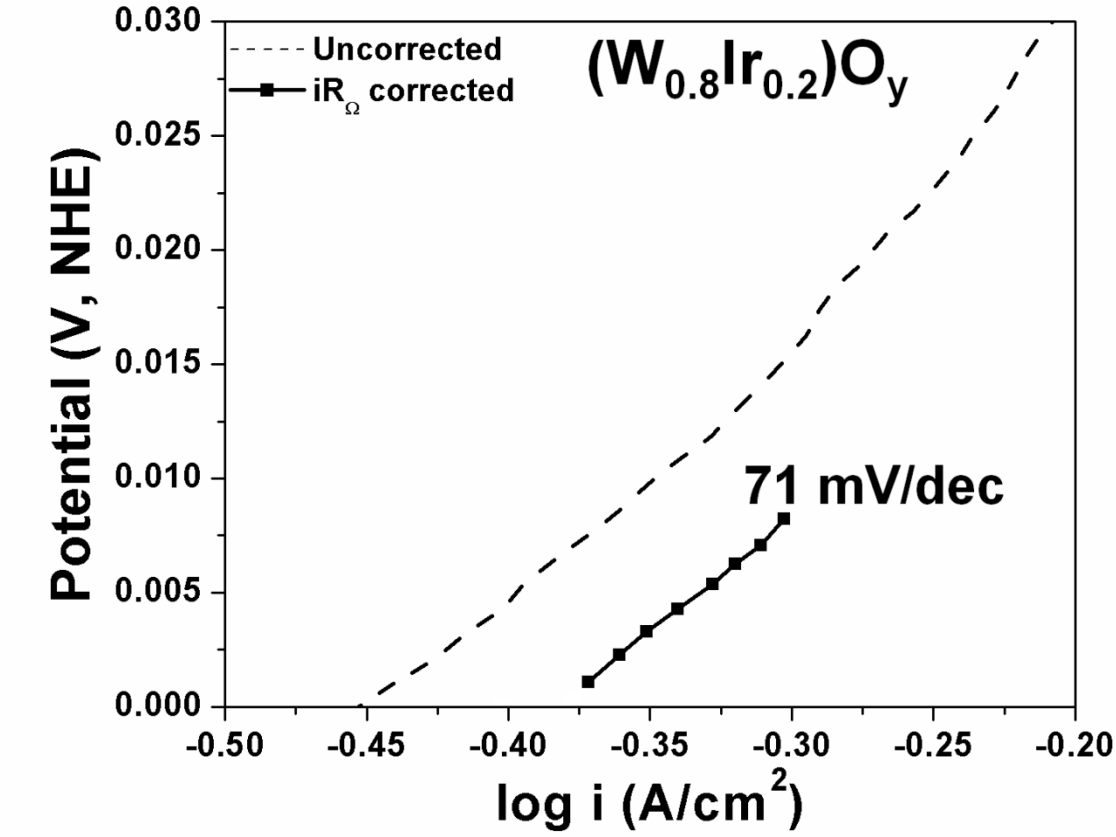

Figure S3: Tafel plot of $(W_{0.8}Ir_{0.2})O_y$, before and after iR_Ω correction.

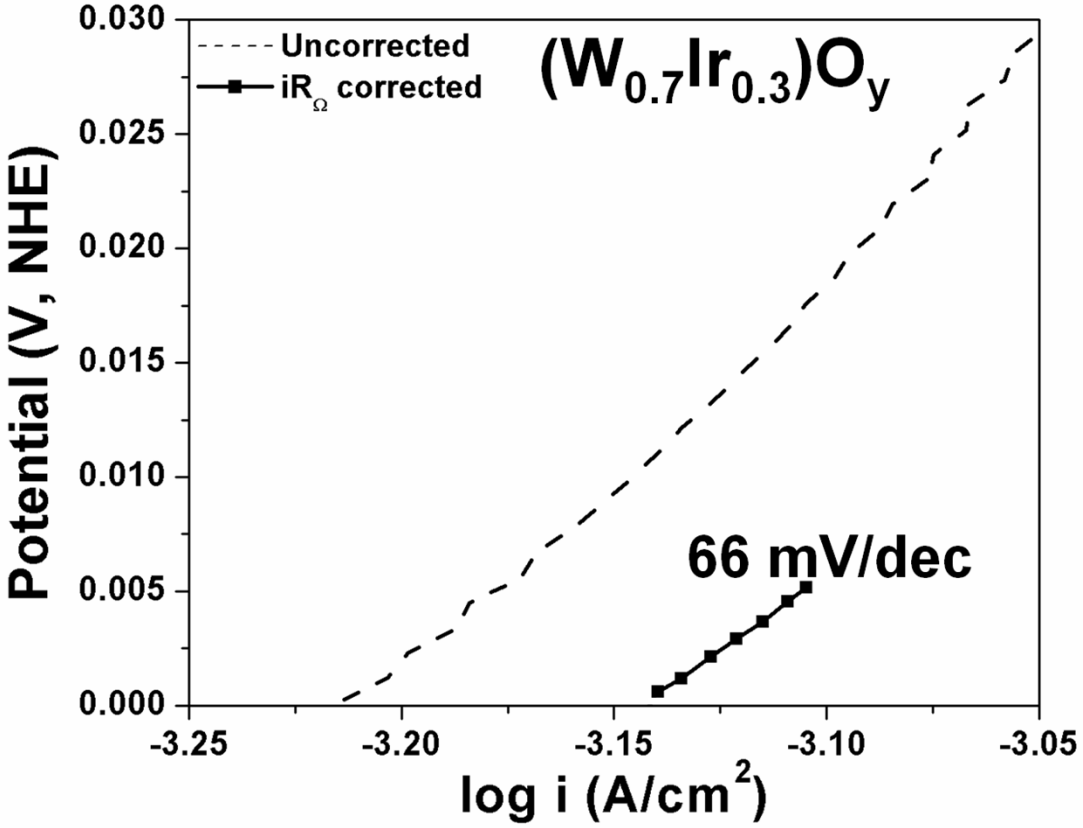

Figure S4: Tafel plot of $(W_{0.7}Ir_{0.3})O_y$, before and after iR_Ω correction.

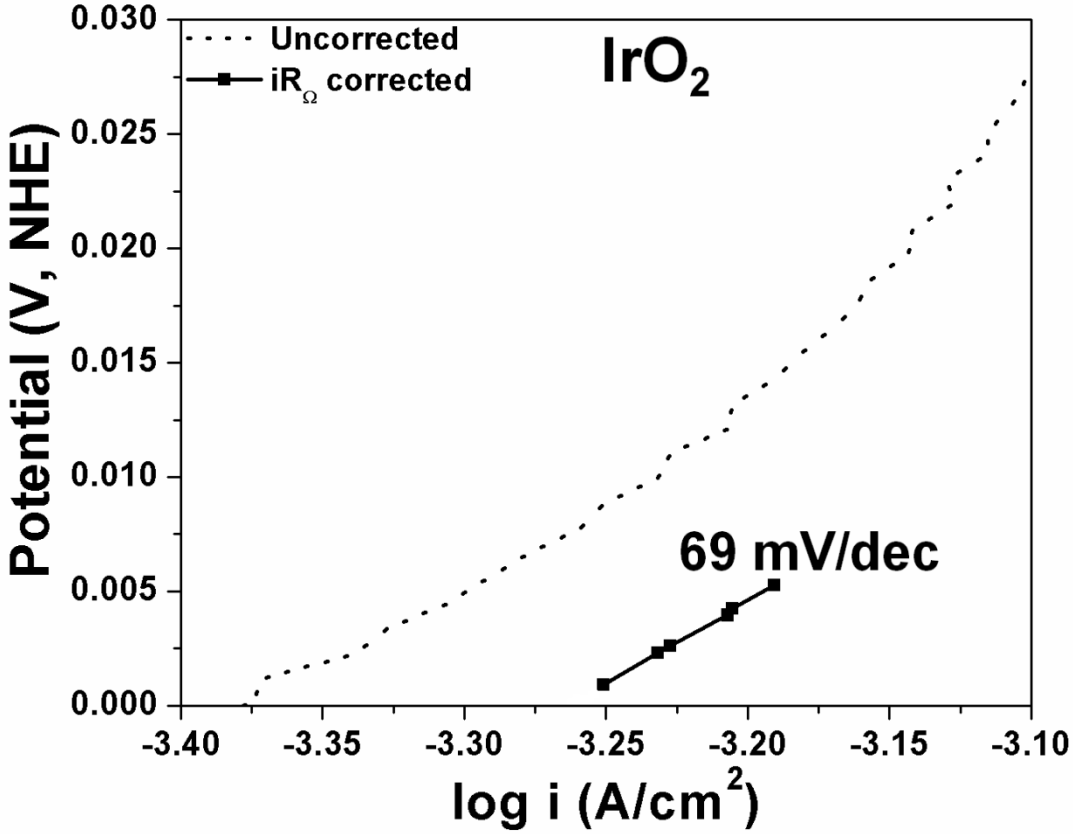

Figure S5: Tafel plot of IrO_2, before and after iR_Ω correction.

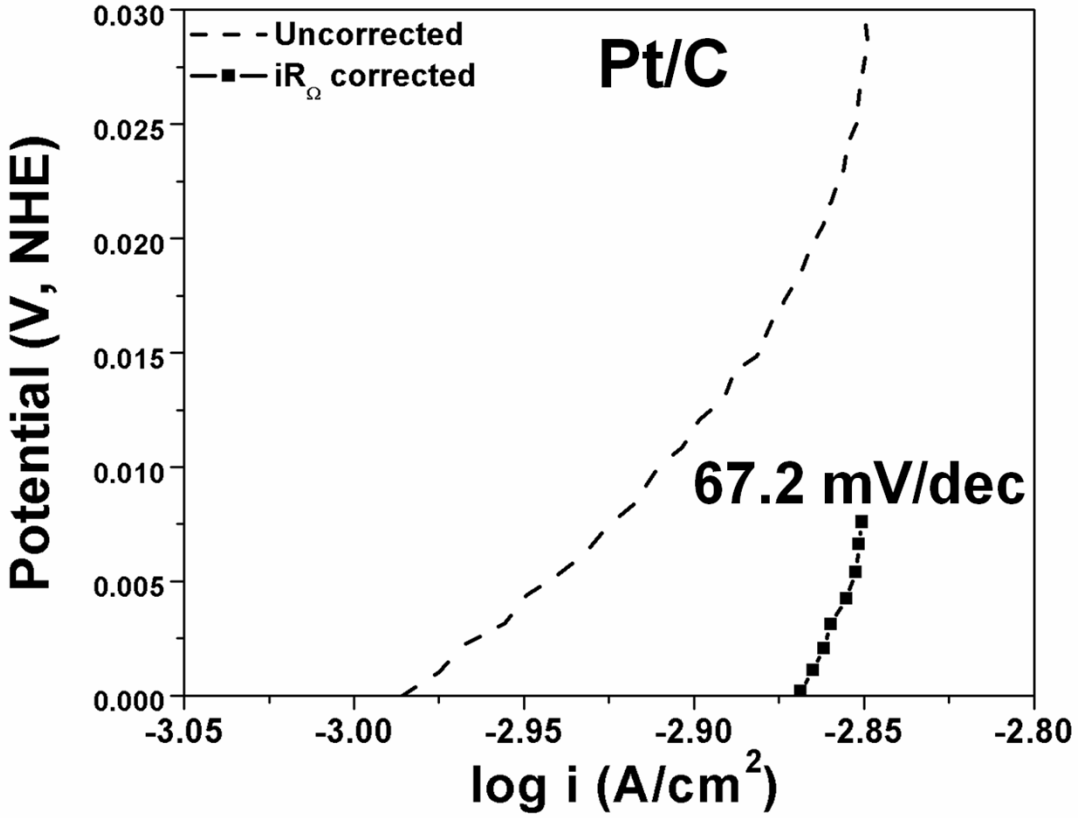

Figure S6: Tafel plot of Pt/C, before and after iR_Ω correction.

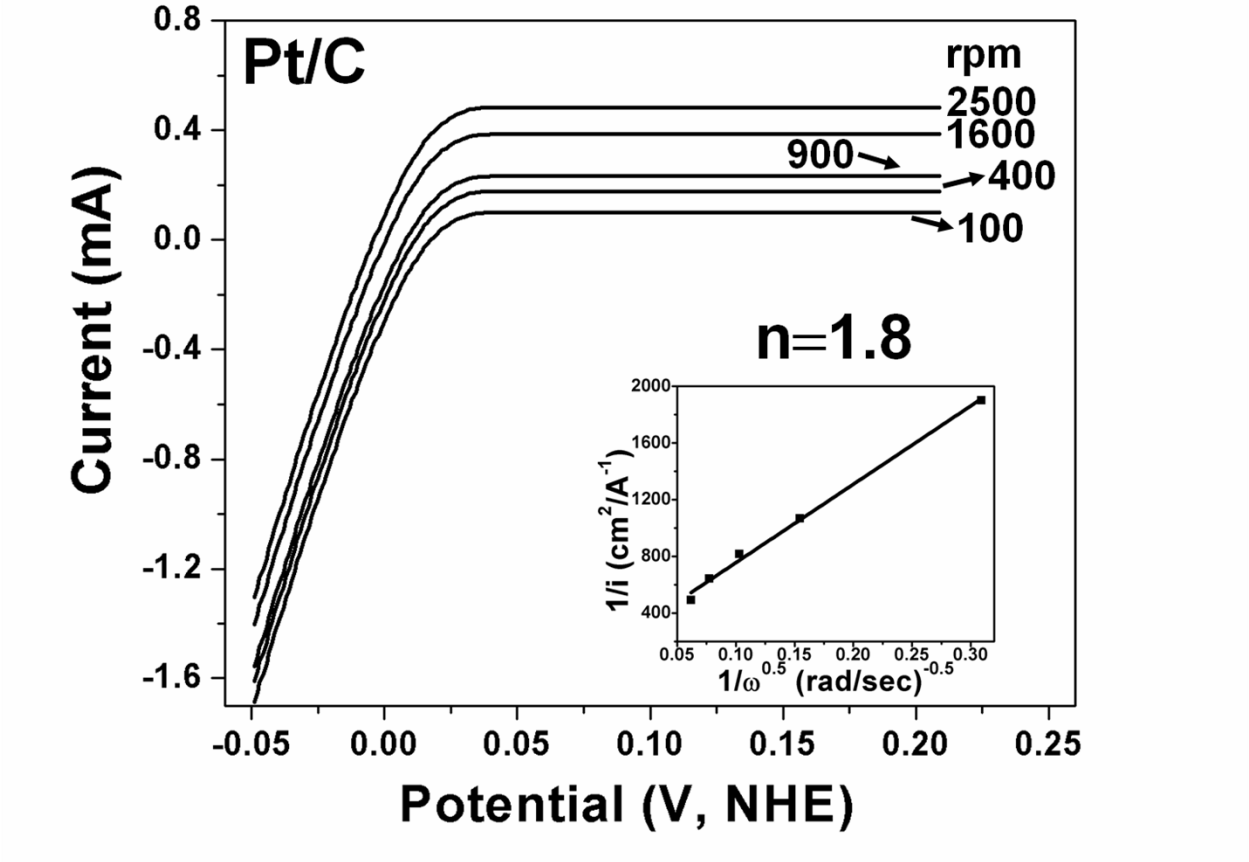

Figure S7: The linear scan voltammogram (LSV) curves for HOR of Pt/C obtained on rotating disk electrode (RDE) at different rotating speeds, measured in H_2 saturated 0.5 M H_2SO_4 solution at 40^0C with a scan rate of 10 mV/sec. Koutechy-Levich plot of Pt/C is shown in the inset of LSV curve.

References:

1. M. Nagarajan, G. Paruthimal kalaignan and G. A. Pathanjali, *International Journal of Hydrogen Energy*, 2011, 36, 14829-14837.
2. P. P. Patel, M. K. Datta, O. I. Velikokhatnyi, P. Jampani, D. Hong, J. A. Poston, A. Manivannan and P. N. Kumta, *Journal of Materials Chemistry A*, 2015, 3, 14015-14032.