

Supporting Information

Fabrication of MEA based on Sulfonic Acid Functionalized Carbon supported Platinum Nanoparticles for Oxygen Reduction Reaction in PEMFCs

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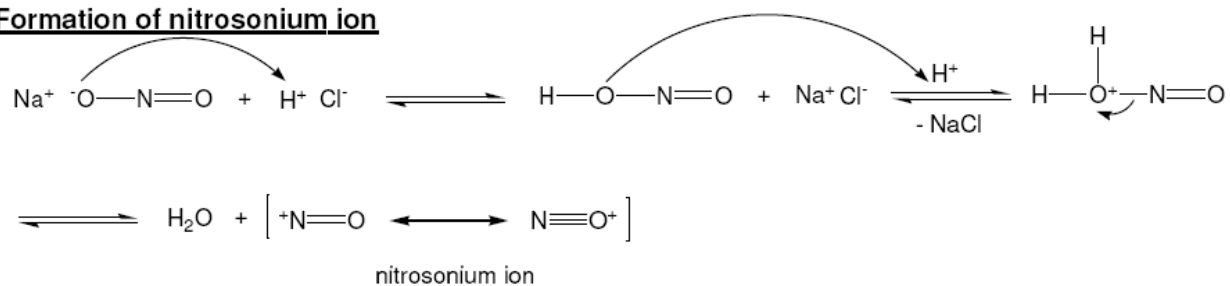
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Formation of nitrosonium ion



Formation of diazotized sulfanilic salt

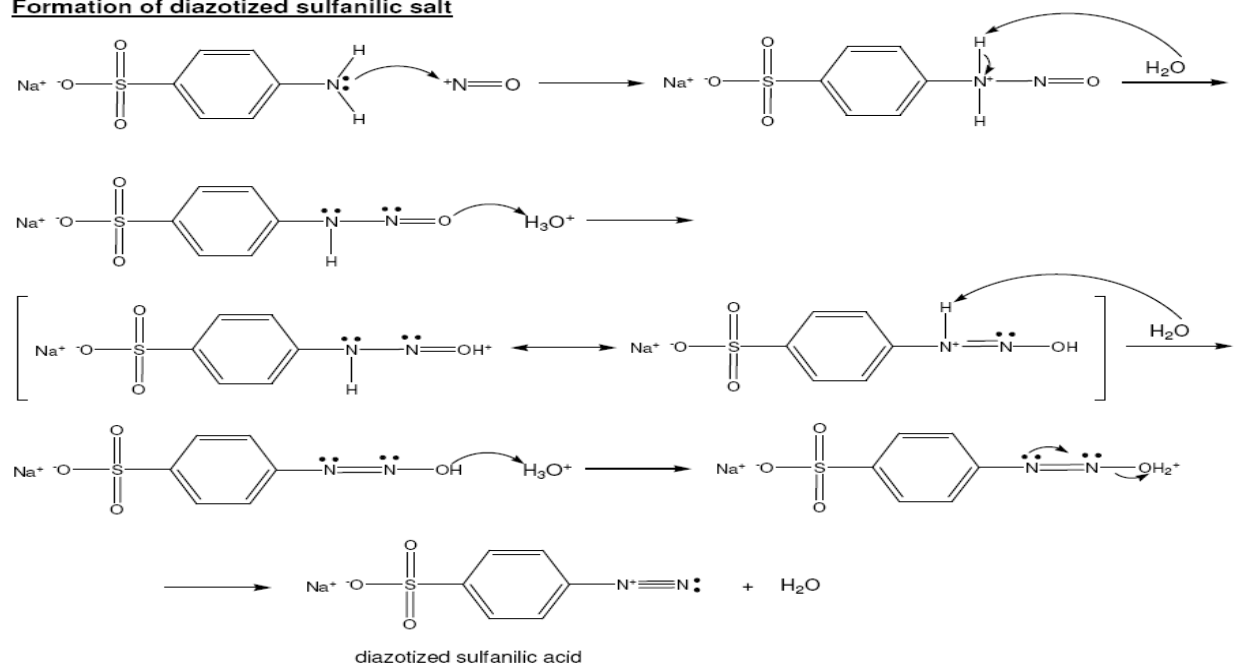


Fig. S1. Schematic diagram for the formation of 4-sulfobenzendiazonim Salts.

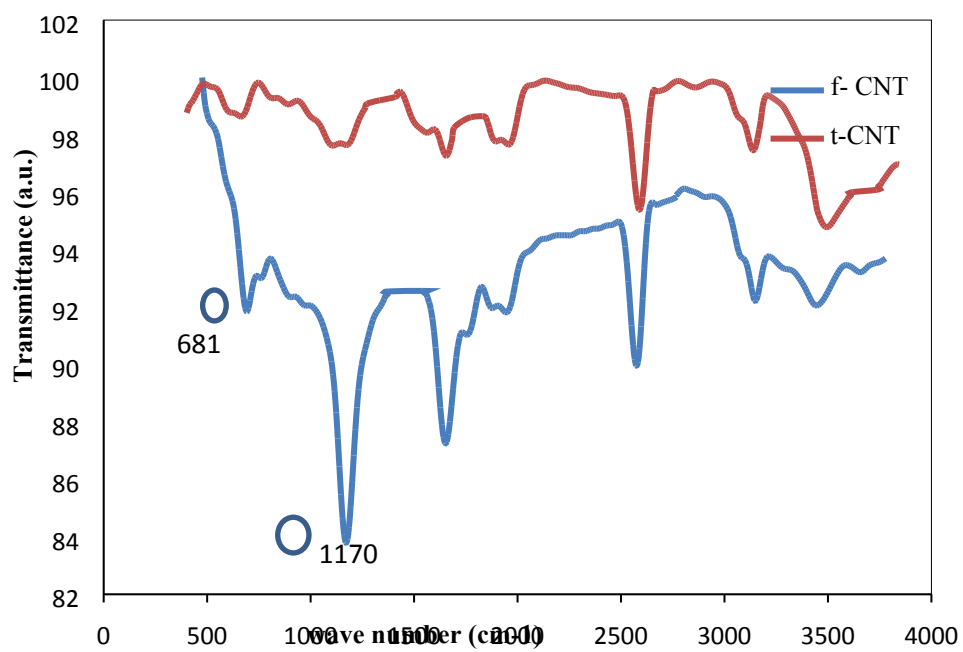
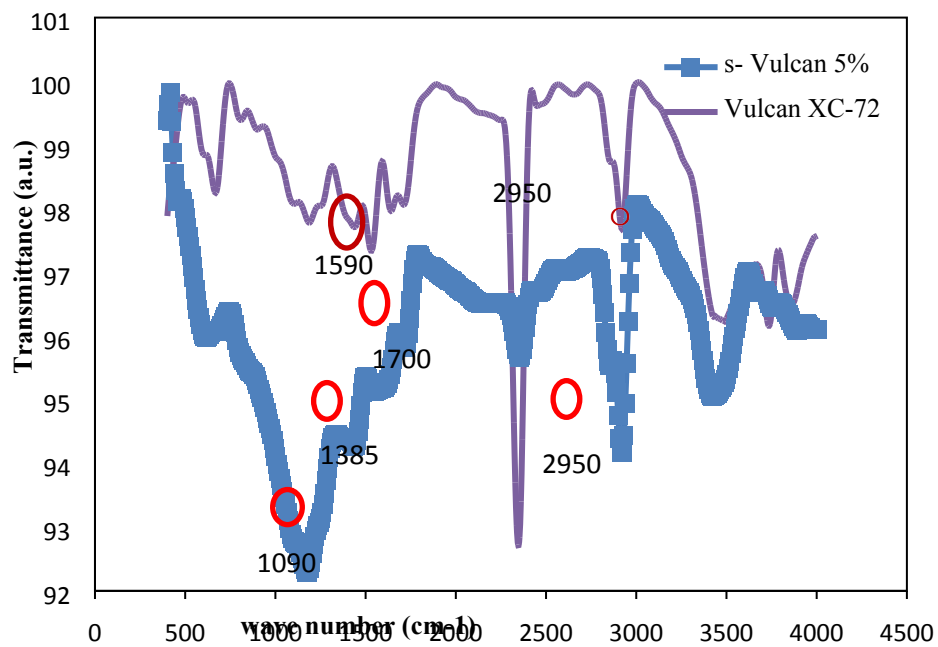


Fig. S2. FTIR spectra for (a) unmodified and modified Vulcan XC-72.
 (b) Purified (t- CNT) and modified (f-CNT) MWCNTs.

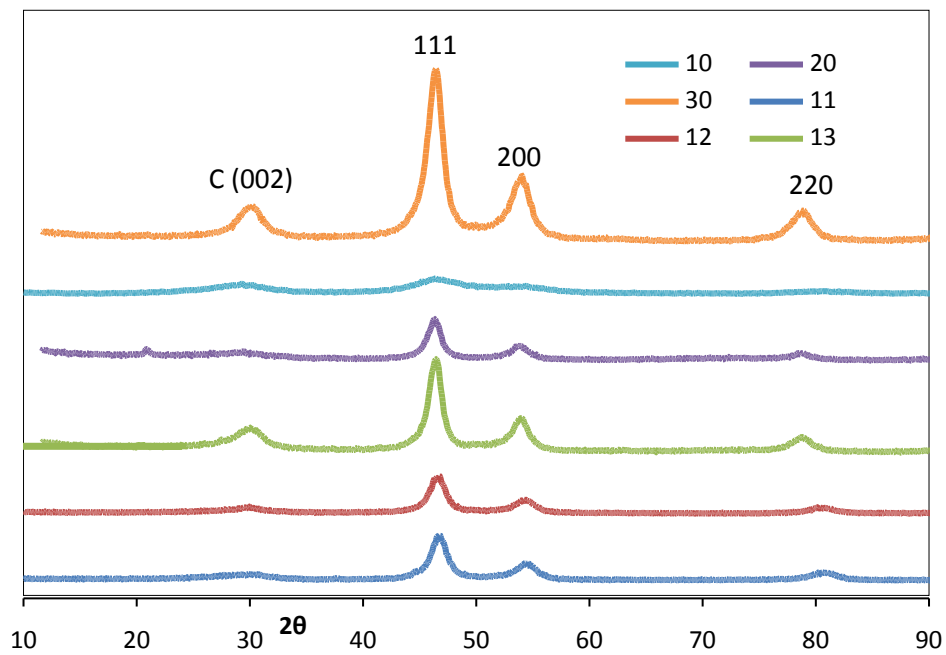


Fig. S3. X-ray diffraction (XRD) patterns for different catalysts.

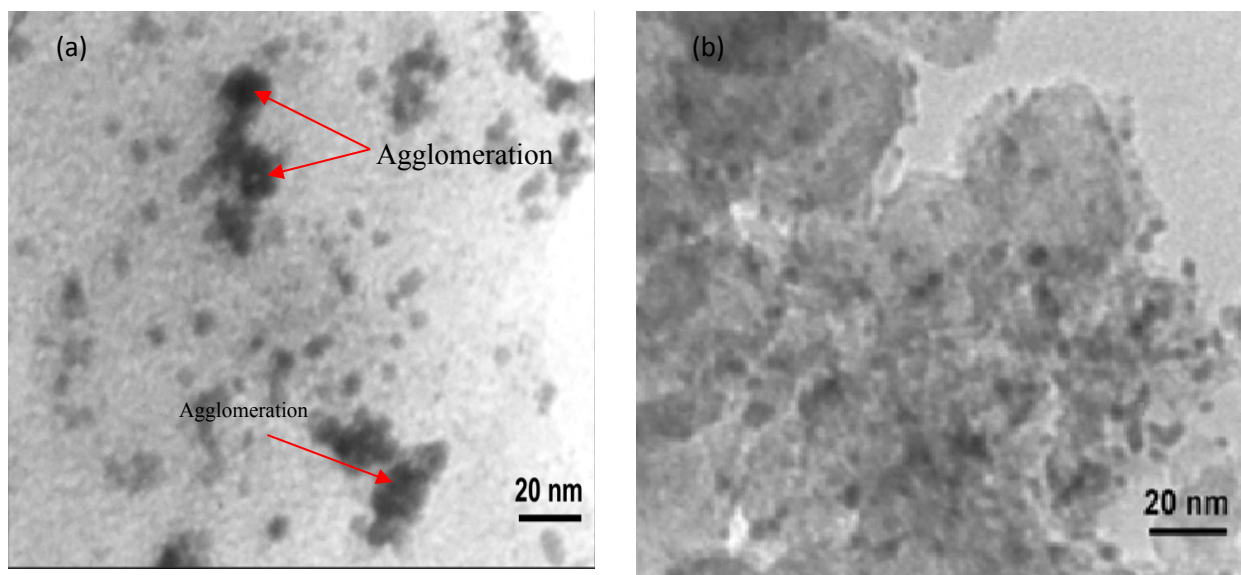


Fig S4. TEM images of (a) commercially available Electrochem Pt/C catalyst (Pt loading 10 wt%). (b) Pt/ (f- Vulcan XC-72R(25%)+f-MWCNT(75%)) catalyst (Pt loading 10 wt%).

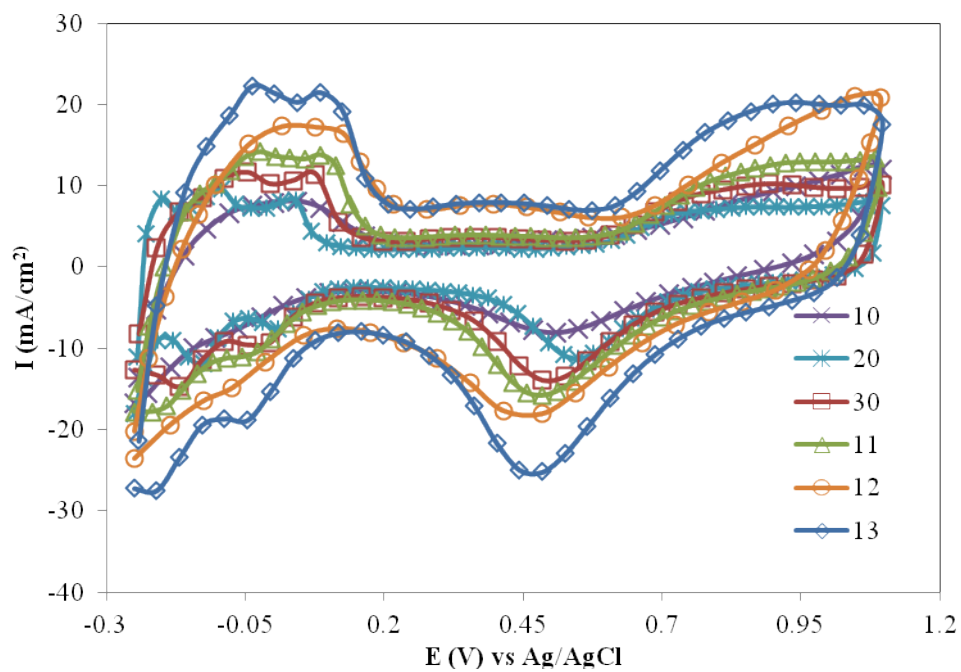
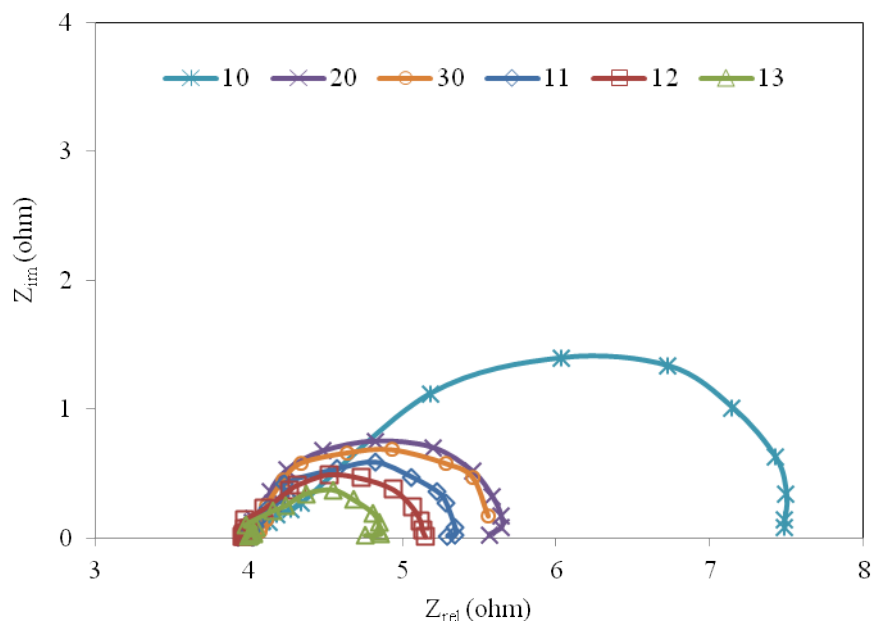


Fig. S5. Cyclic voltammograms for the modified catalyst with varying phenylsulfonic acid loading (in w/o) and amounts of MWCNTs ($0.031415 \text{ cm}^2 \text{ GC}$ at 25°C ; under argon atmosphere; scan rate = 50 mVs^{-1}).



(b)

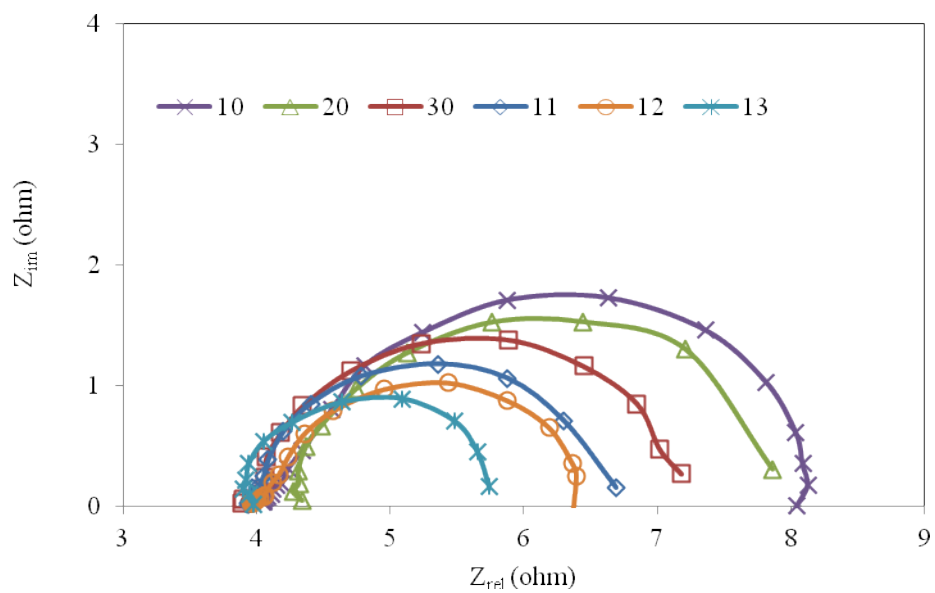


Fig. S6. Nyquist plots of the impedance response from 100 kHz to 30 mHz for different catalysts under oxygen atmosphere (a) at 300 mV (b) at 600 mV vs. Ag/AgCl at 25 °C. (Pt loading: 0.5 mgcm⁻²).

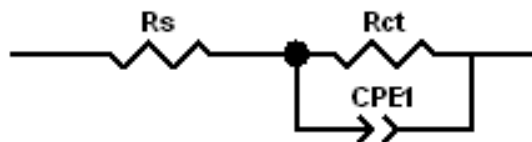
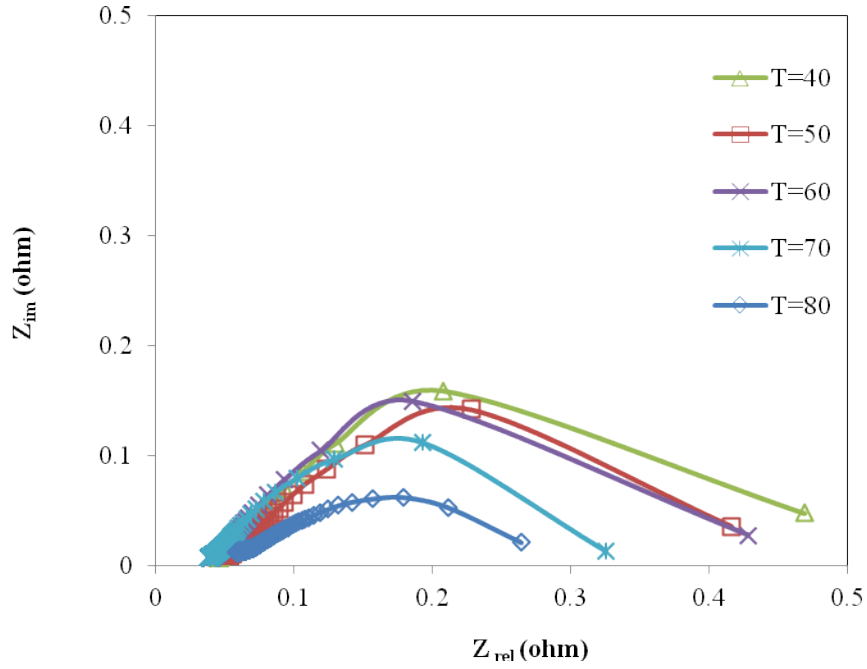
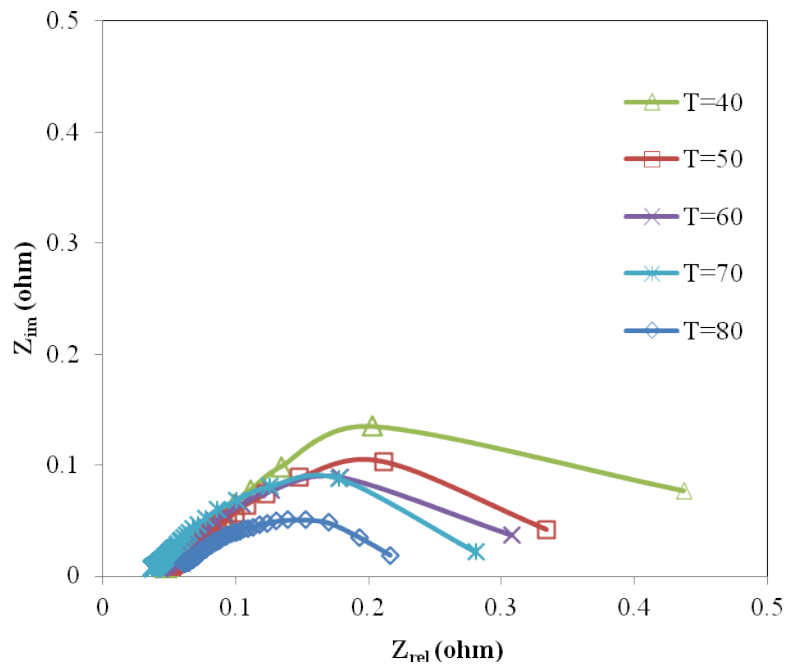


Fig. S7. Schematic representation of the equivalent circuit for the different electrodes.

(a)



(b)



(c)

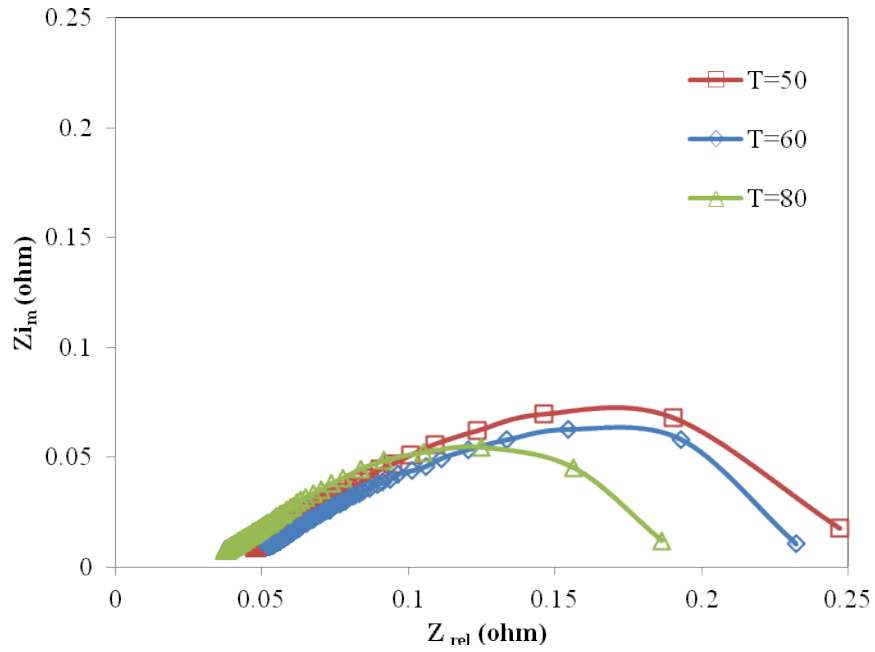


Fig. S8. Impedance spectra of a single cell with MEA-1 from 1 mHz to 1000 kHz , 90% relative humidity, different cell temperatures and 1.5 atm back pressure for the anode and cathode. The flow rates are 300 mlmin⁻¹ for hydrogen and 500 mlmin⁻¹ for oxygen (a) at 0.3V (b) at 0.5 V (c) at 0.7 V.

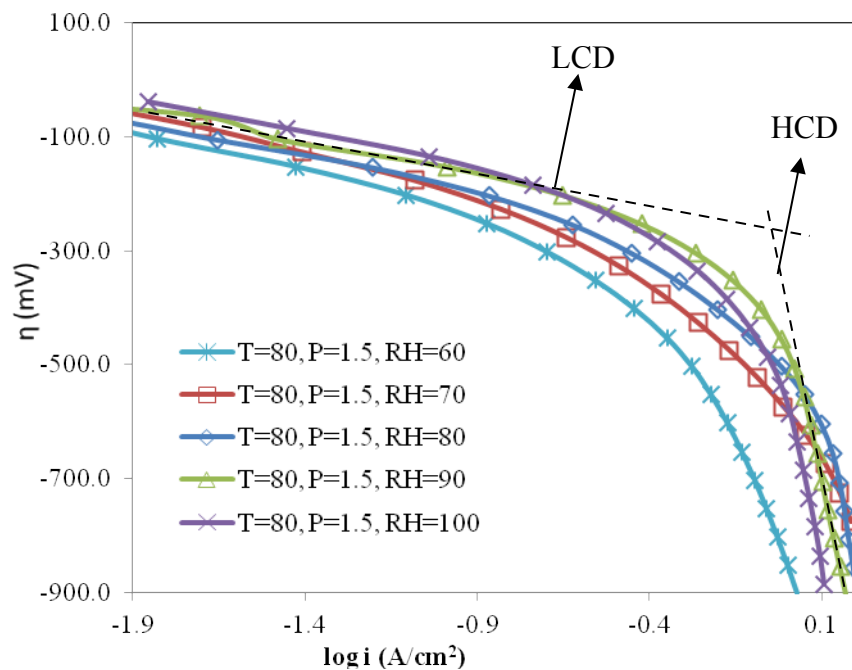
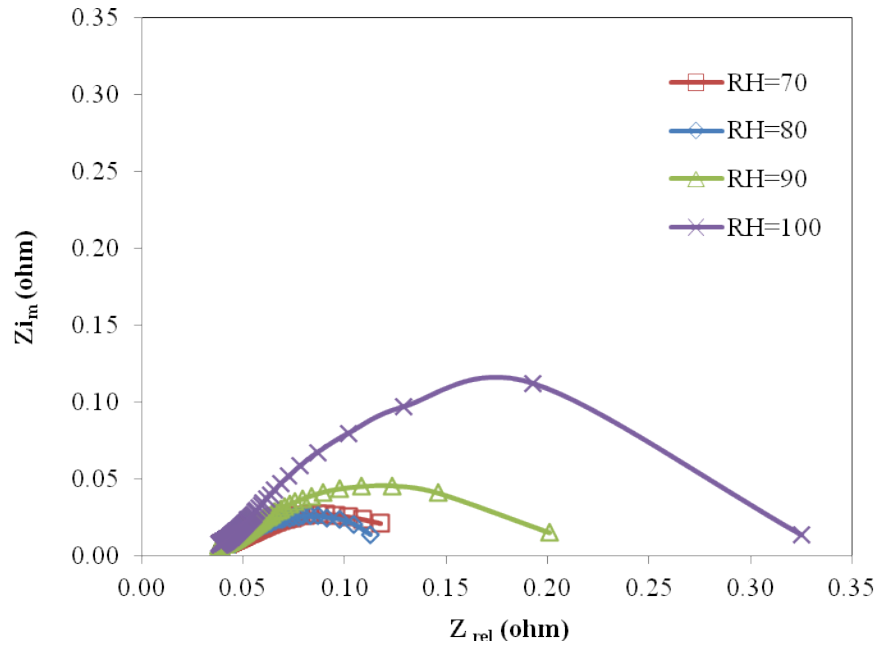
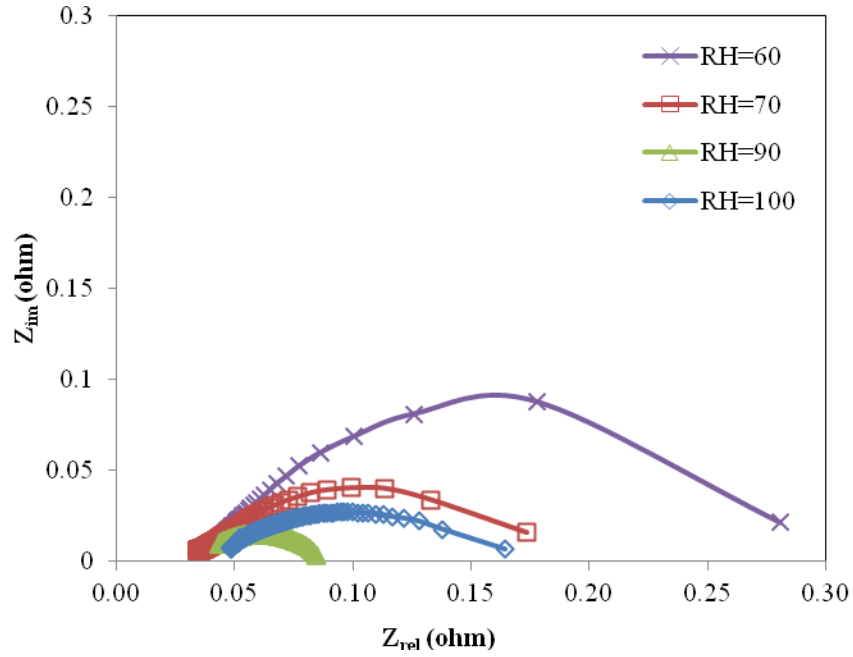


Fig S9. The plot of η vs. $\log i$ for different relative humidities ($T=80^\circ\text{C}$ and a gas pressure at the back of the electrodes of 1.5 atm)

(a)



(b)



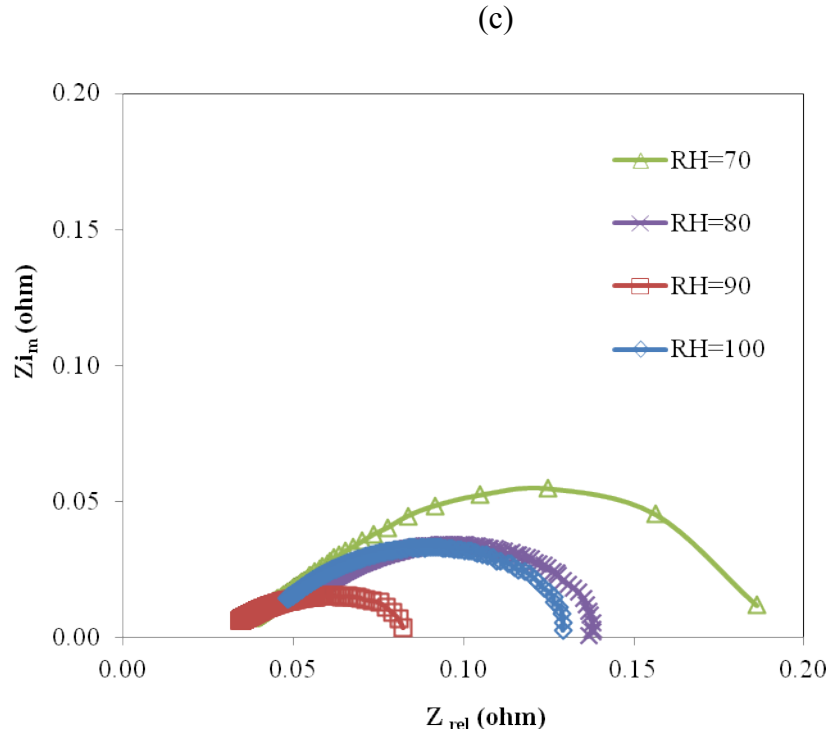


Fig. S10. Impedance spectra of a single cell with MEA-1, from 1 mHz to 1000 kHz, for different relative humidities, cell temperature 80°C and 1.5 atm absolute back pressure for the anode and cathode. The flow rates are 300 mlmin⁻¹ for hydrogen and 500 mlmin⁻¹ for oxygen (a) at 0.3 V (b) at 0.5 V (c) at 0.7 V.

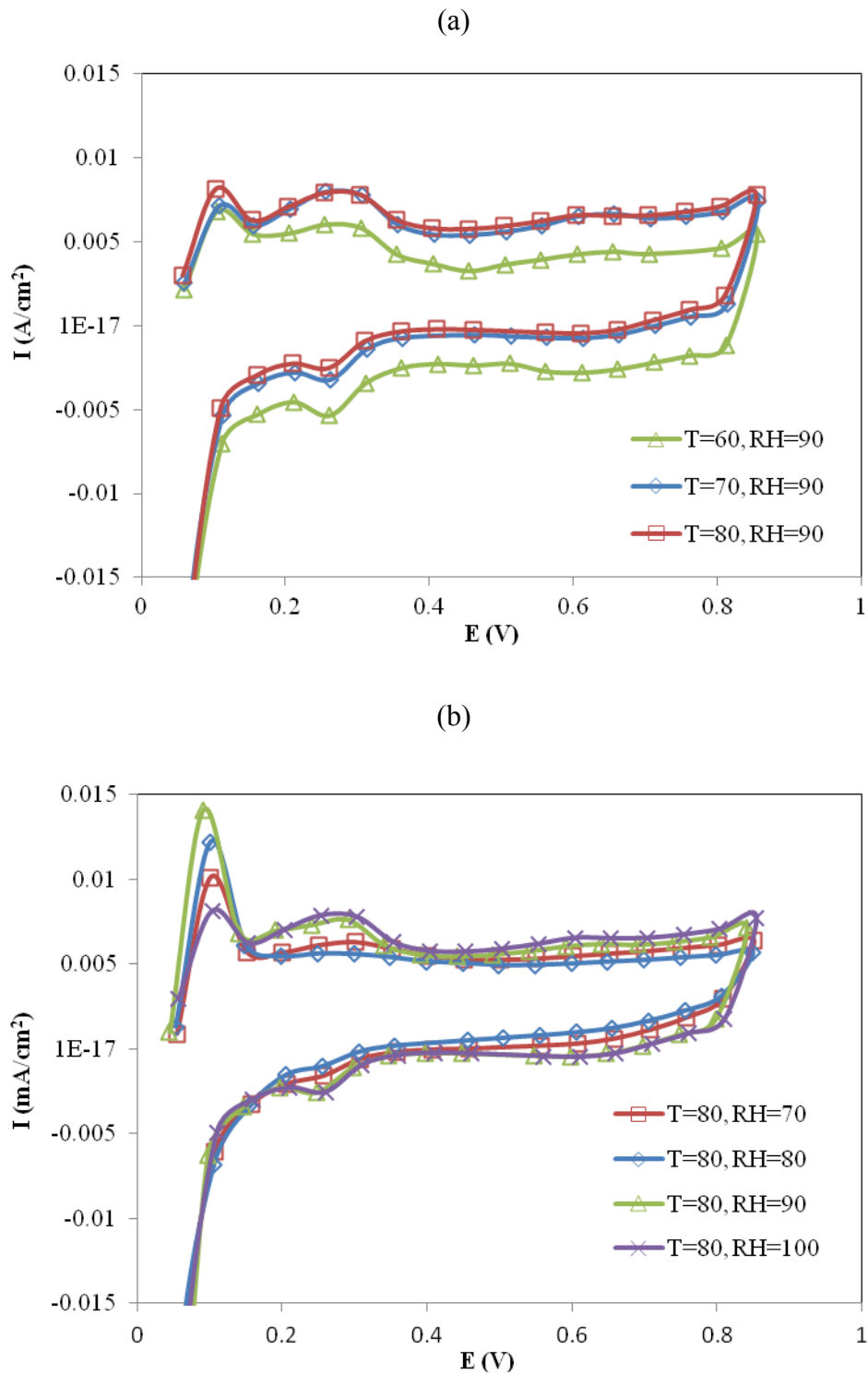


Fig. S11. Cyclic voltammogram of a single cell with MEA-1 (a) effect of temperature (b) effect of relative humidity (RH) (scan rate= 50 mVs^{-1} , cell area: 6.25 cm^2 , N_2 and H_2 streams at cathode and anode, respectively, and an anode and cathode absolute back pressure of 1.5 atm).

Fig. S3. As shown in [Fig. S3](#), the first peak located at a 2θ value of about 30° referred to the graphite (0 0 2) plane of the MWCNT and Vulcan XC-72R support. The other three peaks were characteristic of face centered cubic (fcc) crystalline Pt, corresponding to the planes (1 1 1), (2 0 0), (2 2 0) and at 2θ values of about 46° , 54° , 80° .

Fig. S7. In this circuit, the high frequency intercept on the real axis is due to solution resistance (R_s). A parallel combination of R_{ct} and CPE has been analyzed to form the semicircle, whose diameter has been considered as the charge transfer resistance due to oxygen reduction reaction (ORR) and CPE indicates the double layer capacitance. Considering the porous nature of electrodes, the double layer capacitance is expressed as constant phase elements (CPE) in the equivalent circuit model ³⁶.