

Fig. 12. Activation barrier reduction in the presence of Pt-PANI interlayer.

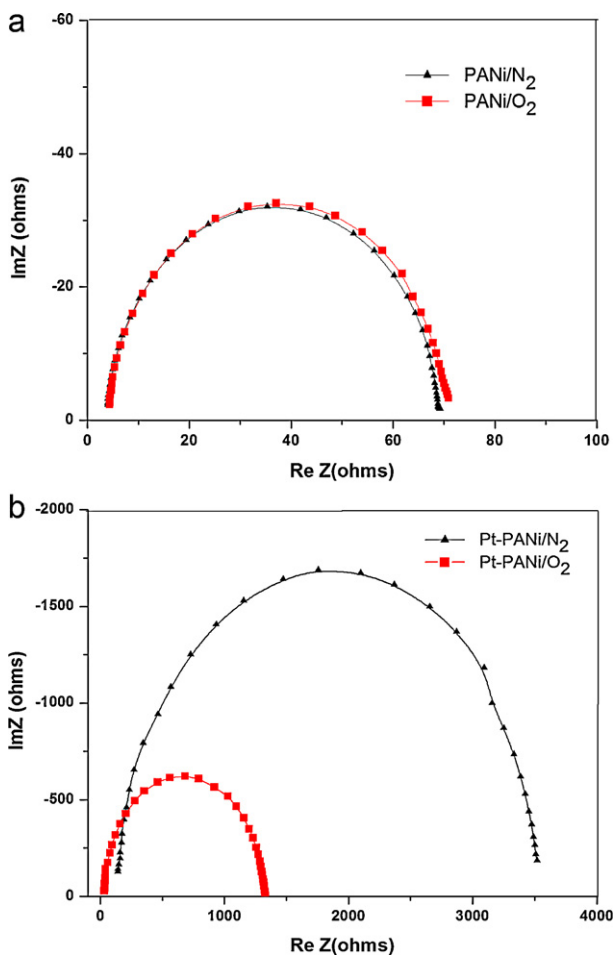


Fig. 13. (a) Nyquist plot of PANi in 0.1 M H₂SO₄ with N₂ and O₂ gases. (b) Nyquist plot of Pt-PANI in 0.1 M H₂SO₄ with N₂ and O₂ gases.

Table 3

Nyquist plot parameters of PANi and Pt-PANI.

System	R_{ct} (Ω)	C_{dl} (μ F)
PANi/N ₂	70	4.57
PANi/O ₂	72	4.44
Pt-PANI/N ₂	3500	0.09
Pt-PANI/O ₂	1300	0.44

Fig. 13a and b illustrate the AC impedance spectra in 0.1 M H₂SO₄ of PANi and Pt/PANI, respectively. A semi-circle in the impedance spectrum shows a particular process, the high frequency arc corresponds to charge-transfer process and the low frequency arc denotes the diffusion process [51]. As the charge transfer occurs between the electrode and the electrolyte, the equivalent circuit of the electrochemical system contains the double-layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) in parallel for the kinetic controlled reaction. The diameter of the semi-circle in the Nyquist plot gives the value of R_{ct} . Left to right portion of the semi-circle denotes the high to low angular frequency. At the peak of the semi-circle, the angular frequency (ω) is related to C_{dl} as below, from which the C_{dl} value is determined.

$$\omega = \frac{1}{R_{ct} \cdot C_{dl}}$$

The high frequency resistance or ohmic resistance (R_s) is invariant for the PANi electrode both in N₂ and O₂ atmosphere (Fig. 13a). Ohmic resistance arises from bulk resistance and from contact resistance. The semicircle, known as the kinetic loop, is due to the interfacial kinetics of reactions and the loop decreases with increased rapidity of the electrochemical kinetics [52,53]. The charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) of PANi in oxygen and nitrogen atmosphere are evaluated and tabulated (Table 3). R_{ct} values for PANi are found to be almost the same in both the atmosphere and same is the case with C_{dl} also. Nitrogen is an inert gas while oxygen can undergo electrochemical reduction. But both of them are showing identical behaviour on PANi electrode. This implies that without any characteristic electrochemical changes, PANi provides an excellent support matrix for the electroactive catalysts. In the case Pt/PANI (Fig. 13b), the intrinsic surface anisotropy [54] due to the presence of Pt appears to affect the contact resistance as revealed by increased ohmic resistance. R_{ct} in nitrogen atmosphere is higher (3500 Ω) than that in oxygen atmosphere (1300 Ω), implying that adsorption of nitrogen occurs and as it does not show any electrochemical reaction, multilayer adsorption imparts high charge transfer resistance and in turn results in low C_{dl} values. Though similar multilayer adsorption can be expected in the case of oxygen also, its low R_{ct} value indicates the electroactivity of the Pt/PANI composite in the presence of O₂ avoiding multilayer build-up and thereby allowing direct electron transfer between the monolayer and the conductive medium [55]. As the GDL interlayer contains only 1% (0.005 mg cm⁻²) of Pt compared with the loading on the cathode, it does not allow the complete electrochemical reaction to take place at the interphase itself, but reduces the activation barrier for the subsequent electrochemical reaction on the cathode side. The high R_{ct} values on the Pt/PANI could be ascribed to the combination of sluggish O₂ reduction and the limited amount of Pt in the interlayer.

The fuel cell performance of Pt/PANI coated GDL is studied at different temperatures (Fig. 14a) and also compared with that of the reference MEA that did not contain Pt/PANI interlayer (Fig. 14b and c). Fig. 14a shows the performance of fuel cell with Pt/PANI coated GDL at 60, 70 and 80 °C. The increase in performance with increase in temperature is as expected and it is due to the kinetically favoured oxygen reduction, increase in ionic conductivity and better management of the product water. Fig. 14b and c show the