

# Solid Carbon-based Electrode for Hydrogen Fuel Cell with Dual Proton and Electron Conductivity

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## ABSTRACT

A solid carbon-based composite electrode made from charcoal powder and nafion binder has been developed with potential application of storage of hydrogen electrochemically that could be utilised in fuel cells for remote area power supply. The developed electrode could be employed to store energy generated by inherently variable renewable sources and hence could act as a continuous power supply source. Such potential candidate electrode, particularly for fuel cell applications, should be both proton and electron conductive. Proton conductivity of the composite electrode was calculated from the measured proton resistance towards the flow of current using electrochemical impedance spectroscopy. Electron conductivity was calculated from the separately measured electron resistance using a standard ohm-meter or multi-meter. The effect of change in humidity on proton and electron conductivity of the composite electrode was examined. The carbon used was a common form of charcoal powder. Perfluorosulfonic acid or Nafion 117 was used as a proton conducting medium within the composite electrode. Proton conductivities in the range of 0.015 - 0.043 S/cm were recorded, while the electron conductivities were in the range of 5.79 – 6.45 S/cm. It was found that the increased level of hydration lead to increase in the proton conductivity, while electron conductivity falls down.

## Keywords

Electrochemical impedance spectroscopy, composite electrode, carbon, nafion, electron conductivity, proton conductivity

## 1. INTRODUCTION

The continuous increase in the concentration level of the green house gases in the atmosphere has lead to the development of a global hydrogen economy goal. Hydrogen, due to its immense energy content, has been recognized as a future fuel. But, development of a safe, simple and economical energy storage system are some of the major challenges to use hydrogen as a future fuel. Conventional hydrogen vessels including high pressure storage systems or cryogenic systems have various restrictions in terms of cost-effectiveness and net-energy losses [Andrews J. et al. 2014; Andrews J. et al. 2008]. One of the promising methods of hydrogen storage is its absorption in materials like metal hydrides but gravimetric densities of less than 2 wt% only have been obtained so far [Beguin F. et al. 2006]. A secondary energy storage system under the name of 'proton flow battery' have been proposed by Andrews and Seif Mohammadi (2014) based on a reversible proton exchange membrane (PEM) fuel cell with an integrated solid-state electrode capable of storing hydrogen in ionic form. Some preliminary results have been reported by these authors on the performance of an experimental proton flow battery using a composite metal

hydride – nafion electrode for storing hydrogen [Andres J. and S. Mohammadi 2014]. But, these obtained results are way less than the desired figures. Also various anomalies were not addressed in the research reports. Another material which has drawn great research interest of the researchers for storage of hydrogen is Carbon [Beguin F. et al. 2006; Blenda-Martinez M.J. et al. 2008; Frackowiak E. et al. 2002; Guterl C. et al. 2005]. For efficient performance it is important for the composite electrode to have dual proton conductivity and electron conductivity on higher side for various applications like in PEM fuel cell [Hynek S. et al. 1997]. The present paper therefore describes a method to measure the proton conductivity of a composite carbon-nafion electrode using EIS technique, also known as Electrochemical Impedance Spectroscopy technique. The electron conductivity of the same electrode is calculated from the measured electron resistance by a standard multi-meter. The effects of the level of hydration of the carbon-Nafion composite electrode on these conductivities are investigated.

## 2. EXPERIMENTAL

The equipment and materials used in the experimental measurement of the proton and electron conductivities are presented in Table 1.

**Table 1. List of equipment and materials used in the present project.**

Sr. No.	Equipment and materials		
	Equipment/materials	Manufacturer	Model/registered product name
1	Charcoal powder	Produced domestically	N.A.
2	Ion exchange membrane	Alfa-aesar	Nafion®117
3	Nafion solution	Sigma-aldrich	5-5 wt% ethanol
4	Electrochemical workstation	RC instruments	RC-EW 100
5	Humidity chamber	Thermdine scientific	TDH-120-SD
6	Oven	Thermdine scientific	EO-30G

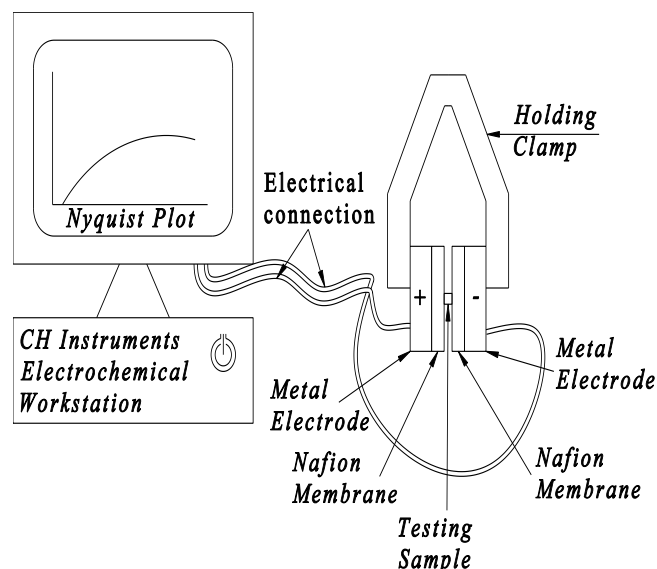
Charcoal in a powdered form is a porous material with range of pores with different diameters viz. macropores, mesopores, micropores and ultramicropores, and is considered as an active candidate for solid hydrogen storage. Therefore, carbon

in form of charcoal powder mixed with nafion-117 solution (perfluorosulfonic acid) was chosen as the material to fabricate the composite carbon-nafion composite electrode. The carbon-nafion solution was stirred well to obtain a slurry mixture. The obtained slurry mixture was then poured into a mould to attain the desired shape. In stirring process, the solvent got evaporated in which the nafion ionomer was dissolved. The mould containing this mixture was kept at room temperature for 8 hours, and then heated in an electric oven at 105 – 110°C for two hours, to evaporate the solvent and form the solid electrode. The carbon-nafion composite electrodes obtained from the mould were exposed to atmospheres with different relative humidity to hydrate the electrodes to various levels. Five samples named as Carbon-N-RC, Carbon-N-RH35, Carbon-N-RH75, Carbon-N-RH100 and Carbon-N-WC with specifications shown in Table 2 was prepared. Sample CN-RC was stored in room conditions (relative humidity around 60%) for 24 hours. Samples Carbon-N-RH35, Carbon-N-75 and Carbon-N-100 were stored in a humidity chamber maintained at 35%, 75% and 100% relative humidity respectively. Sample Carbon-N-WC was stored in de-ionized water for 24 hours before testing. All the fabricated samples were later used to measure their proton resistance by electrochemical impedance spectroscopy technique. To measure the proton resistance, each sample was placed between two nafion-117 membranes backed by two gold-plated metal electrodes in, as shown in Figure 1. The usage of the two nafion membranes on both sides of the composite electrode ensured there was no direct electrical (that is, electron) current between the two electrodes of the EIS instrument, given that the composite electrode is itself a good electron conductor. The two nafion membranes used in the set-up were made from a single piece of nafion-117 membrane treated with  $H_2SO_4$  and boiled in de-ionized water to remove dirt, grease and stains and hence to obtain a clear membrane for testing. The cleaned membrane was cut in two pieces to match the size of the gold-plated metal electrodes which are to be used in the EIS technique. Two gold-plated metal electrodes were cleaned with acetone and ethanol in order to remove any accumulated dirt or grease. The positive and negative leads of the EIS workstation were applied to the overall test assembly (Figure 1). Nyquist plots, i.e.  $Z'$  vs  $-Z''$ , were obtained for frequencies varying from 0.1 Hz to  $10^6$  Hz.

**Table 2. Specifications of the prepared samples.**

Sample	Condition	Width of Sample in cm	Length of Sample in cm	Area in $cm^2$ 'A'	Thick ness in cm 'Th'
		W	L	A = W x L	
Carbon-N-RC	Room Condition	0.120	0.515	0.0618	0.075
Carbon-N-RH35	RH – 35%	0.56	0.44	0.2464	0.075
Carbon-N-RH75	RH - 75%	0.59	0.24	0.1416	0.075

Carbon-N-RH100	RH – 100%	0.45	0.477	0.2165 4	0.075
Carbon-N-WC	Wet condition	0.55	0.446	0.2453	0.075



**Fig 1: Measurement of proton resistance of the samples using Electrochemical Impedance Spectroscopy technique**

Proton resistances were obtained from the EIS technique, as the high-frequency intercepts on the real impedance ( $Z'$ ) axis were used to calculate proton conductivity of the sample along with their cross sectional areas and thicknesses. The tests were repeated with all samples i.e. Carbon-N-RC, Carbon-N-RH35, Carbon-N-RH75, Carbon-N-RH100 and Carbon-N-WC, and hence their respective proton conductivities were calculated. A standard ohm-meter was employed to measure electron resistance using outer electrodes that had the same cross sectional area as the sample electrodes. Hence electron conductivity for all five different samples was calculated using the known dimensions of the electrodes.

### 3. RESULTS AND DISCUSSIONS

When the AC voltage is applied through the electrochemical workstation in the frequency range of 0.1 to  $10^6$  Hz, a Nyquist plot is obtained as shown in Figure 2 for the CN-RC electrode. The intercept of the Nyquist plot on the higher frequency end of the curve is a measure of the total series resistance (real component of the total impedance). This intercept can best be estimated from the zoomed view of the high frequency end of the Nyquist, as shown in Figure 3. The proton resistances of the nafion membranes were measured separately using EIS. The measured proton resistances of nafion membranes and resistances of the gold-plated metal electrodes employed in the setup were subtracted from the total proton resistance of the whole setup to obtain the proton resistance of the sample.

The Nyquist plot and zoomed view for the Carbon-N-RH35, Carbon-N-RH75 and Carbon-N-RH100 samples are shown respectively in figures 4 to 9 and the corresponding plots for the Carbon-N-WC electrode are given in figures 10 and 11.

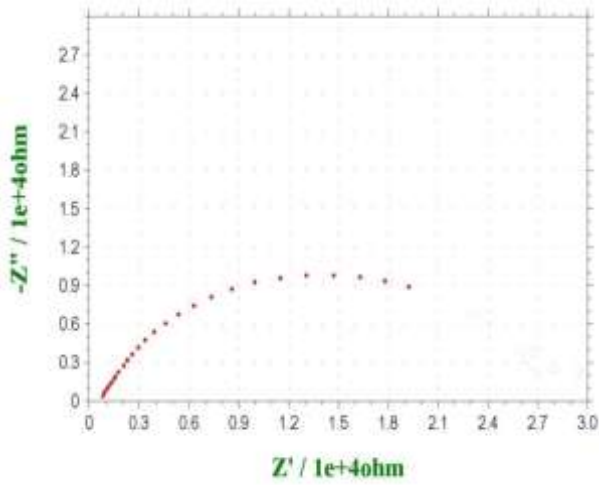


Fig 2: Nyquist plot for the composite electrode sample Carbon-N-RC.

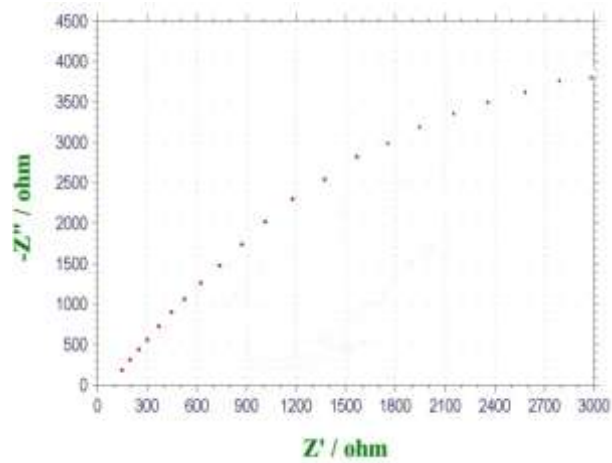


Fig 3: Zoomed view of the Niquist plot for composite electrode sample Carbon-N-RC.

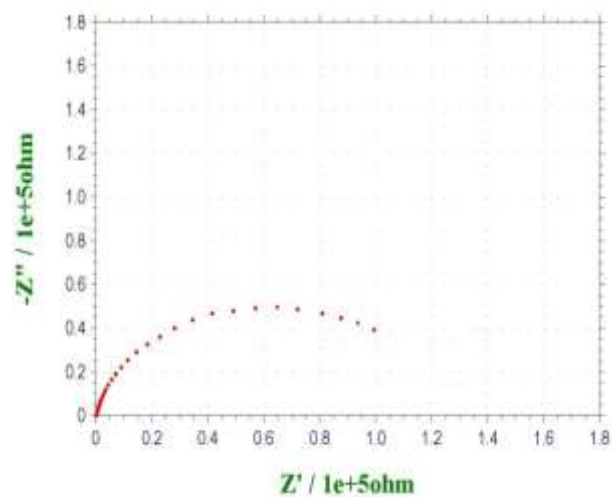


Fig 4: Nyquist plot for the composite electrode sample Carbon-N-RH35.

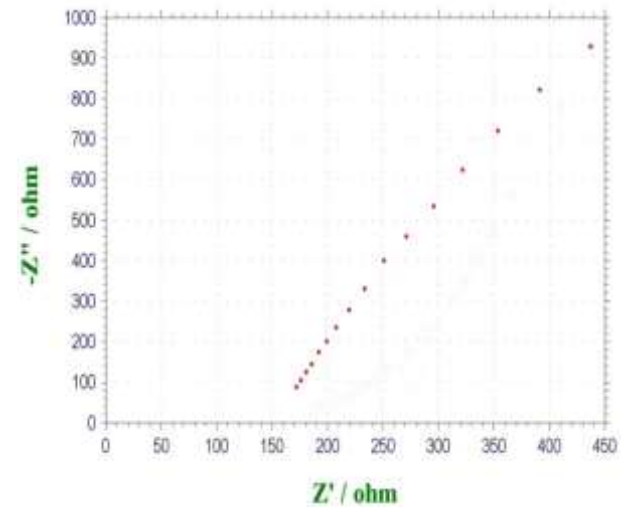


Fig 5: Zoomed view of the Niquist plot for composite electrode sample Carbon-N-RH35.

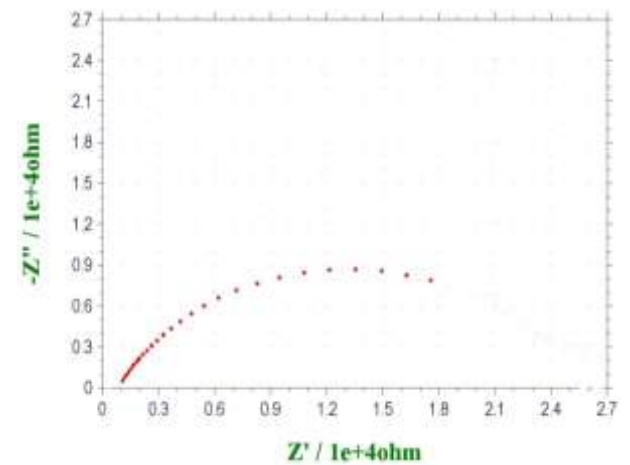


Fig 6: Nyquist plot for the composite electrode sample Carbon-N-RH75.

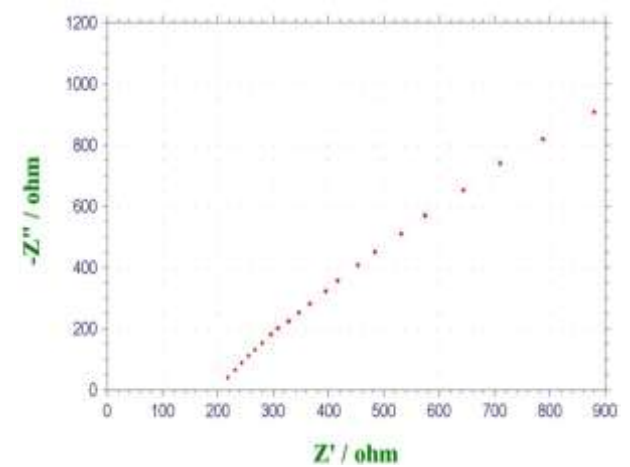


Fig 7: Zoomed view of the Niquist plot for composite electrode sample Carbon-N-RH75.

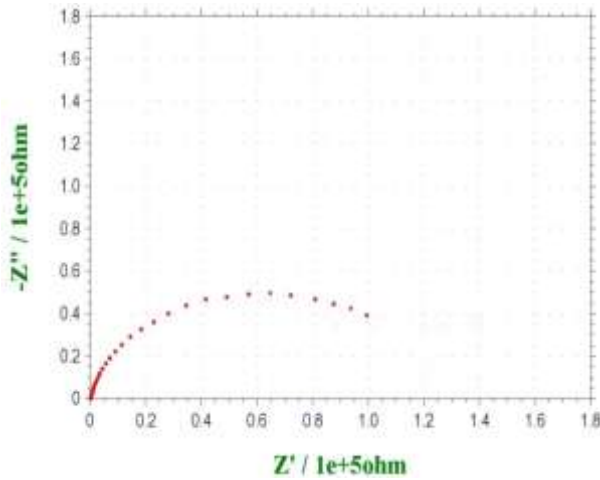


Fig 8: Nyquist plot for the composite electrode sample Carbon-N-RH100.

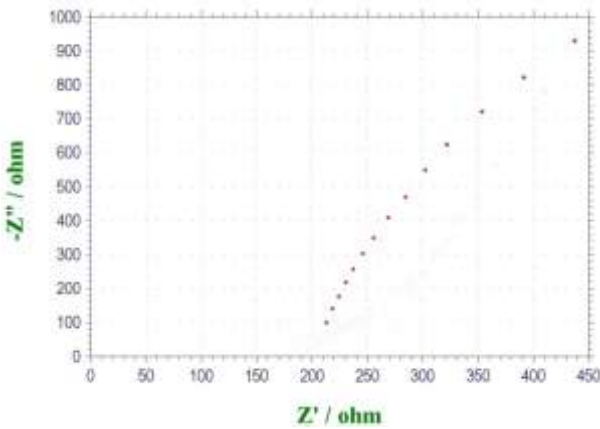


Fig 9: Zoomed view of the Nyquist plot for composite electrode sample CN-RH100.

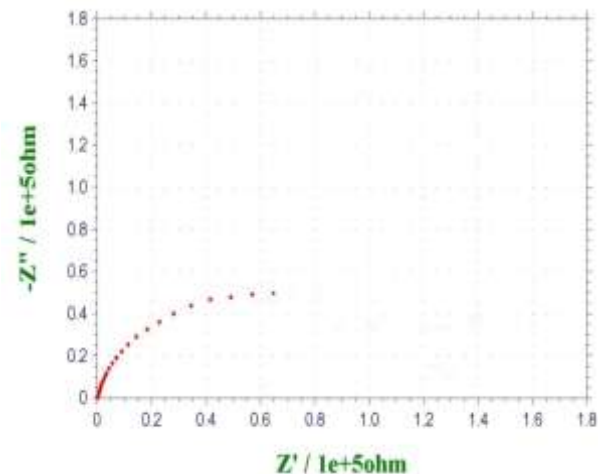


Fig 10: Nyquist plot for the composite electrode sample Carbon-N-WC.

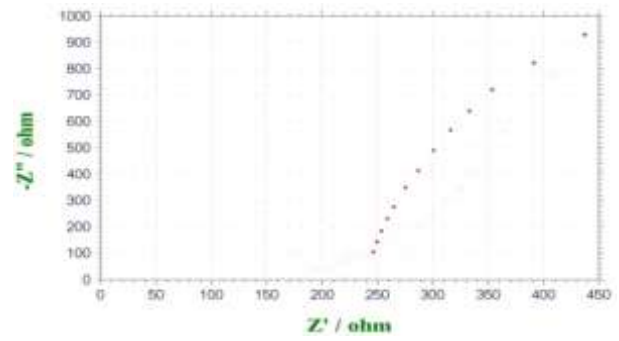


Fig 11: Zoomed view of the Nyquist plot for composite electrode sample CN-RH100.

The proton conductivities for all samples at differing levels of hydration obtained by this method are presented in Table 3. The proton conductivities of the electrodes were calculated from their known cross sectional areas, thicknesses and measured proton resistances across the electrodes using the following equation:

$$\sigma_p = t / A \times R$$

where;  $\sigma_p$  = proton conductivity of the sample

$t$  = thickness of the sample

$A$  = area of the sample

$R$  = proton resistance of the sample

At room condition the proton conductivity of the electrode was found to be less (equal to 0.014775 S/cm) as compared to the electron conductivity (equal to 6.45 S/cm). As the level of hydration of the electrode goes up at relative humidity of 35%, the proton conductivity rises (equal to 0.020465 S/cm) and the electron conductivity gets lower (equal to 6.28 S/cm) as compared to the respective conductivities at room conditions. Under wet conditions, the proton conductivity further rises up (equal to 0.042273 S/cm) and electron conductivity gets further down (equal to 5.79 S/cm). The electron conductivity directly across each electrode was calculated by the measured electron resistance using a standard ohm meter and is given in Table 3, along with the corresponding calculated proton conductivities.

Table 3. Proton and electron conductivity of the samples.

Sample	Proton conductivity of the sample in S/cm ' $\sigma_p$ '	Electrical conductivity of the sample in S/cm ' $\sigma_e$ '
Carbon-N-RC	0.014775	6.45
Carbon-N-RH35	0.020465	6.28
Carbon-N-RH75	0.030718	6.01
Carbon-N-RH100	0.037269	5.85
Carbon-N-WC	0.042273	5.79

#### 4. CONCLUSION

The proton conductivity of the composite Carbon-nafion electrode rose 0.014775 to 0.042273 S/cm with increasing hydration. The measured electron conductivities recorded were in the range 5.79 to 6.45 S/cm, and were found to fall with increasing hydration. The increase in proton conductivity with more water content is consistent with the usual behavior of nafion. A possible explanation of the fall in electron conductivity with increasing hydration is that nafion swells as its water content increases, so that the area of contact between the C particles embedded in the nafion is likely to be diminished. Importantly for their potential application in a proton flow battery and in other areas, the composite C-nafion electrode made and tested in this study has shown acceptable levels of both proton and electron conductivity.

#### 5. REFERENCES

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