

ACTIVATED CARBON AS POROUS JUNCTION FOR REFERENCE ELECTRODES

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SUMMARY: A piece of activated carbon was prepared from coconut shell and used as a porous junction in a reference electrode. The rate of leakage of electrolyte from the reference electrode into the test solution was measured. Its use in actual pH measurements indicated good response.

Key Words: Activated carbon, porous carbon, reference electrode junction.

INTRODUCTION

Activated carbon is structurally different from graphite because of the presence of pores of various sizes. It was shown (1) that water could seep into these pores and at the same time increase the conductivity of activated carbon from $\sim 1 \times 10^{-6}$ to $\sim 7 \times 10^{-6} \text{S}$. Since the pores penetrate carbon throughout, water can flow from one end to the other with the rate of flow dependant upon its inclination (3). The transport of material was found to be very slow. For a downward flow of water through a vertically positioned piece of carbon of 15 mm length, for example, the time taken for carbon to reach its maximum conductivity was at least 20hrs at 33°C. Hence, activated carbon can be used as a porous junction material for a reference electrode in an electro-chemical measurement which requires very low leak.

Several materials have been used for porous junctions (8) using several techniques (9,11). The present communication describes our attempt to introduce yet another material to replace the commonly used sintered glass. In addition to the fact that activated carbon is the principle material under investigation in our laboratory, it is also readily available and its source, the coconut shell, is a common agricultural byproduct in many Islamic countries. Industrial utilization of such byproducts is a major goal of our research activities.

MATERIALS AND METHODS

Large pieces of activated carbon were prepared from coconut shell by a method described earlier (10). They were refluxed in 1M HCl for a week and washed with distilled water in a Soxhlet apparatus for a week. They were then dried at 70°C in an oven. A small piece was ground with fine sand paper into a cylindrical rod of about 1.8 mm diameter and 5.5 mm length. An activated carbon junction for a reference electrode was prepared by sealing the carbon rod into a borosilicate glass tubing of 2 mm diameter with Araldite epoxy resin. A sample of the carbon was analyzed for impurities by nuclear activation analysis (NAA) and its pore size was estimated by scanning electron microscopy (SEM).

Two additional porous junctions were prepared for the purpose of comparison. A sintered glass junction was obtained by removing the calomel electrode from a Beckmann reference electrode. A paper junction was prepared using a slight modification of the method described by Shoemaker and Garland (9); the sliver of Whatman Qualitative 3 filter paper was sealed into position using Araldite epoxy resin since the leak rate of the electrolyte was found to be unacceptably high when grease was used as sealant. All three junctions were filled with saturated KCl solution and soaked in distilled water for at least one week before use.

Each junction was tested for electrolyte leak in the following manner. A small Calomel electrode obtained from a broken TOA combination electrode was inserted into the prepared junction. This electrode and a Chemtrix glass electrode were placed in a 3-neck round bottom flask (250ml) containing distilled water

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(200 ml). The water was stirred using a magnetic stirrer. The circuit was completed to simulate pH measurement. The rate of leak of KCl through the porous junction over a period of 6.5 hours was observed by following the increase in the conductivity of water between two Pt electrodes connected to a Wynne-Kerr Autobalance Universal Bridge B642. The quantity leaked was calculated as the difference between the initial and final concentrations of K⁺ in the water as determined by atomic absorption spectrophotometry.

A piece of activated carbon was immersed in distilled water. The conductivity of the distilled water was followed for a period of 6 hours in a control experiment.

pH measurements were also carried out using the prepared junctions. These were done by placing a glass electrode together with all three junctions in HCl and NaOH solutions of various concentration. The calomel electrode was inserted in turn into each of the junctions and the readings on a TOA HM-7B pH meter were recorded for each concentration of the acid and base.

The experiments were repeated using an Ag/AgCl elec-

trode in 1M HCl, another reference electrode commonly used in electrochemical measurements. The Ag/AgCl electrode was prepared according to Shomaker and Garland (9). The quantity leaked was calculated as the difference between the initial and final concentrations of H⁺ in the water as determined by titration with standard base.

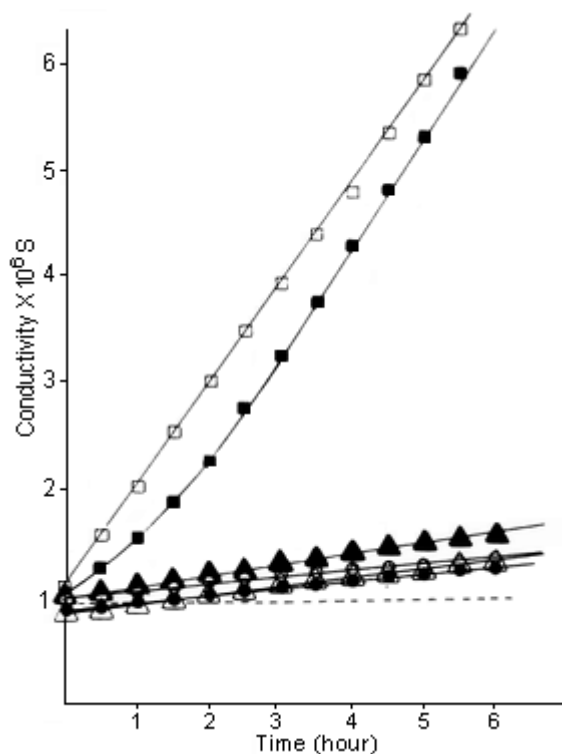
RESULTS AND DISCUSSION

In these experiments we have assumed that the initial concentration of ions in the distilled water did not influence the rate of leakage of KCl and HCl from the reference electrodes. The assumption appeared to be correct as indicated by the linearity of the rate of increase in the conductivity of the water (Figure 1). Hence, no effort was made to purify the distilled water samples to a common degree, but the values reported in those figures are of the same order of magnitude given elsewhere (6).

Since activated carbon was produced from an agricultural byproduct, it is reasonable to expect some inorganic impurities to be present. Table 1 gives the concentrations of some elements that could be detected by NAA in any appreciable amount in one of the samples. All the values were very low and comparable to the requirements of living plants (4). However, the total percentage was slightly higher than that found earlier by ashing (2). Regardless of the amount present, these impurities seemed to have very little effect on the conductivity of water as shown by the results of the control experiment as given in Figure 1. Any adsorbed impurities would be removed by the rigorous washing and cleaning, leaving only those that were intercalated in the lattices of the graphite crystallites. Mere soaking during the experiment did not result in migration of intercalated impurities from the lattice into the water. Thus the increase in the conductivity of the distilled water in the presence of the junctions was due to leak of KCl and HCl from the reference electrode only.

The transport of material from the reference electrode into the distilled water took place through the pores of the junctions. In the case of activated carbon, these pores vary in size (7) and are distributed all over the carbon surface and penetrate it throughout. The electron micrograph, Plate 1, illustrates some pores measuring about 10 microns in diameter. Even though carbon is hydrophobic, the presence of functional groups along the wall of the pores (5) facilitate the flow of water through them. Thus since the reference junction was filled with an electrolyte, water could seep into these pores, carrying the ionic species.

Figure 1: Conductivity of water as a measure of rate of leaks of internal reference electrode solutions.



- ▲: Paper junction with Saturated KCl
- △: Paper junction with HCl (IM)
- : Carbon junction with Saturated KCl
- : Carbon junction with HCl (IM)
- : Beckman junction with Saturated KCl
- : Beckman junction with HCl (IM)
- ...: Control

Table 1: Impurities in Carbon.

%			ppm				
Na	K	Ca	Al	Cl	Br	As	Sb
0.012	0.21	0.03	20	70	0.2	0.1	0.04

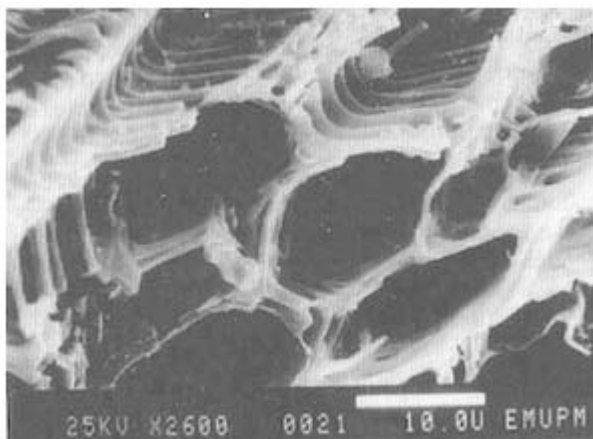
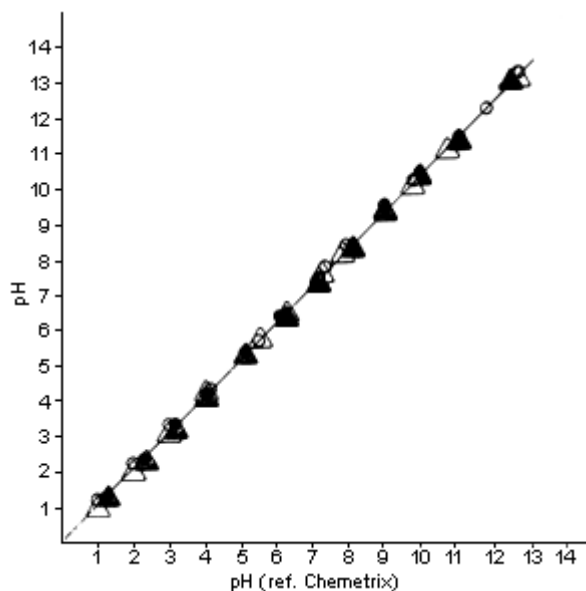


Plate 1: Electron micrograph of pores in activated carbon.

As the ionic species diffused from the pores of the junctions into the distilled water, the conductivity of the latter increased. The rates of increase were very small 8.78×10^{-7} , 1.03×10^{-7} S per hour respectively for sintered glass, filter paper and carbon. In absolute terms, the rates were 0.99, 0.35 and 0.25 ppm, respectively. It is interesting to note that the rate obtained for filter paper junction was very similar to that for carbon. In this case, the epoxy resin probably soaked the paper thus constricting the pores. However, rates obtained for both junctions were found to be lower than that for the commercially available sintered



- ▲: Paper junction with HCl (IM)
- △: Paper junction with Saturated KCl
- : Carbon junction with HCl (IM)
- : Carbon junction with Saturated KCl

Figure 3: Comparative pH measurements.

glass. Thus, these materials, especially carbon, are suitable for use in an electrochemical measurement in which ionic contamination of the sample should be avoided.

pH measurements were carried out using the same reference electrode inserted in turn into each of the three junctions against a glass electrode. Figure 2 shows that there was virtually no difference in the accuracy of the measurements.

CONCLUSION

The cheapness of carbon and its ready availability favour the use of the material as reference junction in the construction of reference electrodes. The slow rate of leak makes the junction especially useful in electrochemical measurements which require minimization of contamination.

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