

Effect of surface oxygen complexes of sugar charcoal on the half cell potential of carbon-nickel ferrite electrodes

N K SANDLE and G VASUDEV

Department of Chemistry, Indian Institute of Technology, New Delhi 110 029

MS received 2 May 1979

Abstract. Carbon-nickel ferrite electrodes were prepared by pressing equal amounts of charcoals and nickel ferrite using ABS polymer (in acetone + benzene) as binder on a steel mesh. The half cell potentials reported were measured with reference to saturated calomel electrode. The electrolyte used was 4-N potassium hydroxide and fuel used was methanol. The surface oxygen complexes on the charcoals were varied (i) by heat-treating the sugar charcoal in vacuum at 400, 750 and 1000° C and (ii) by boiling in 4N.HNO₃ for different intervals of time. Half cell potential measured increases with the increase of oxygen content of the charcoals. The oxygen complex which is disposed off as carbon dioxide imparts polarity to the charcoal surface, and is largely responsible for the increase in potential.

Keywords. Oxygen complexes; sugar charcoal; cell potential; carbon-nickel ferrite electrodes.

1. Introduction

It is well realised that the surface properties of charcoal are largely influenced by the chemisorbed oxygen. It has been shown by Puri *et al* (1956, 1963, 1964) that charcoal surface is usually covered by two types of oxygen complexes, one of which on degassing decomposes to give CO₂ and the other as CO. The first complex (CO₂-complex) imparts polarity, acidity and hydrophilic character, while the second complex is largely inert. Carbons have been used extensively as electrode materials in alcohol-air or -oxygen fuel cells but a literature survey indicates that the effect of the extent and nature of surface oxygen complexes of carbons on the electrode potential have not been studied systematically. The electrode potential of electrodes prepared by using different carbon samples having varying amounts of surface oxygen complexes were therefore studied and this paper describes the results of our studies on the electrodes prepared by using sugar charcoal prepared by carbonisation of cane sugar. The results obtained by using sugar charcoal activated by (I) degassing it at 400, 750 and 1000° C, (II) by heating with 4N HNO₃ for different intervals of time, i.e., 30 and 60 min are reported.

2. Experimental

2.1. Preparation of charcoals

Sugar charcoal was prepared by carbonising recrystallised cane sugar with conc. H_2SO_4 . The char obtained was washed free of sulphate ions, dried and powdered. The sugar charcoal thus obtained referred as original sugar charcoal in the text was degassed in vacuum at 400, 750 and 1000° C in the manner described earlier by Puri *et al* (1956). A known weight of original sugar charcoal was treated with 4N HNO_3 for different intervals of time, i.e., 30 min and 1 hr. The treated samples were washed with distilled water till free from traces of acid.

2.2. Preparation of nickel ferrite

Nickel ferrite was prepared by mixing NiO , and Fe_2O_3 in equal proportions, and fired at 1000° C for 1 hr. The sample thus obtained was tested for ferrite formation.

2.3. Preparation of electrodes

Equal proportions of charcoal and nickel ferrite were mixed. The above mixture was made into a paste with an ABS binder dissolved in acetone and benzene and then painted on a stainless steel mesh (150 mesh). This was allowed to dry and sandwiched by mechanical pressing.

2.4. Measurement of cell potential

The electrodes prepared as above were used as cathodes in a cell assembly shown in figure 1. The half cell potentials were determined with reference to a saturated calomel electrode. The electrolyte used was 4N potassium hydroxide and the fuel used was methanol (100 ml 4 N KOH + 10 ml CH_3OH). The potential was measured with an Aplab digital multimeter model 1003 (± 1 mV) at room temperature.

3. Results and discussion

The oxygen present on the surface of the carbon was analysed (Puri *et al* 1956). The results given in table 1 indicate that as the temperature of degassing is increased, the amount of oxygen on the carbon surface decreases. The sugar charcoal having 25% oxygen loses most of this oxygen when heated to 1000° C. Treating charcoal with nitric acid results in increasing the amount of oxygen chemisorbed (i.e., from 25% to 35%). These results of 400, 750 and 1000° degassed samples are comparable with Puri *et al* (1963). Nitric acid treated sample show an interesting behaviour. Most of the increase in the chemisorbed oxygen appears to be in the form of CO_2 -complex. The increase in the oxygen which comes off as CO is only marginal and there is no increase in the amount of oxygen which comes off as water.

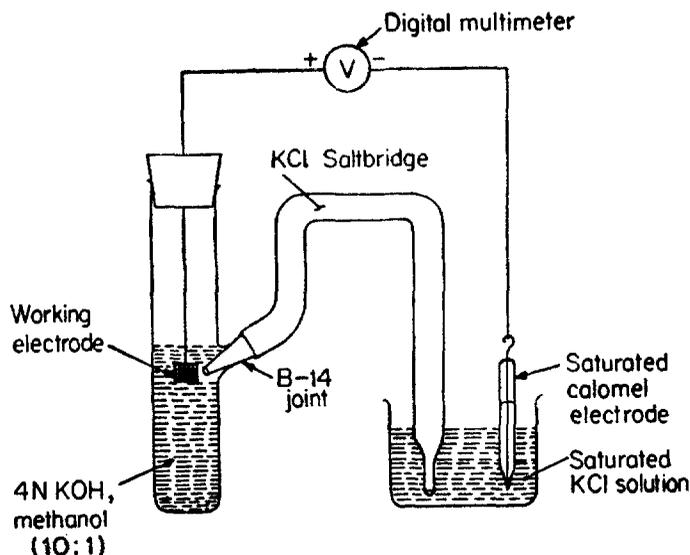


Figure 1. Cell assembly for the measurement of half-cell potential.

The results of the half cell potentials measured by using different types of charcoal given in table 2 show that the original sugar charcoal has the maximum half cell potential, i.e., 587 mV. In 400° and 750° degassed charcoals the value decreases to 472 and 190 mV respectively. The half cell potential of the electrode prepared by using pure nickel ferrite measures 449 mV, which is less than the value for original sugar charcoal but more than the value of 400 and 750° degassed sugar charcoals. This decrease in between original sugar charcoal and degassed charcoal appears to be due to the loss of the oxygen complex capable of decomposing as carbon dioxide. Puri *et al* (1956) has called this as CO₂-complex, as this complex is well known to impart polarity and hydrophilic behaviour to the surface. The increase in half cell potential is understandable. The complexes capable of decomposing as carbon monoxide have been reported to be inert (Kipling and Wright 1968). Other factors like surface area also do not appear to affect the potential values much, since surface areas of all these degassed samples as reported by Puri and Bansal (1965) do not change very much by increasing the temperature of activation and remain around 390-400 m²/g.

The results of the half cell potential of the electrodes prepared by mixing equal proportions by weight of charcoal and nickel ferrite are given in table 3. The results indicate that values are minimum in 1000° degassed charcoal-ferrite electrodes and maximum in HNO₃-treated 60 min charcoal ferrite electrode. On comparing the results of the electrode prepared from original charcoal with the electrodes prepared from the mixture of different charcoals and ferrites it is seen that the half cell potential of the later type of electrodes is lower than that of the pure charcoal electrodes.

The normalising effect of the mixing of ferrite with charcoal does not play a significant role as the experimental values are not the arithmetical means. The decreasing trend can be explained only with more experimental data. However,

Table 1. Disposition of oxygen on the activated and nitric acid treated sugar charcoal.

Sample	Gases evolved on evacuation at 1200° C (mg/g)			
	CO ₂	CO	H ₂ O	Total oxygen
Original sugar charcoal	151.1	129.3	80.6	255.5
400° degassed sugar charcoal	58.3	119.3	57.5	161.7
750° degassed sugar charcoal	Nil	97.0	15.1	103.4
1000° degassed sugar charcoal	Nil	10.0	Nil	5.7
HNO ₃ treated for 30 min	201.5	140.0	80.0	309.0
HNO ₃ treated for 60 min	268.6	139.0	80.0	346.8

Table 2. Half cell potential of the electrode made by using different types of sugar charcoals.

Charcoal sample used	Half cell potential	
	in pure KOH (mV)	in KOH + MeOH (mV)
Original sugar charcoal	587	450
400° C	472	454
750° C	109	155
Nickel ferrite	449	380

the effect of varying the oxygen content of the charcoal appears to be more predominant. The 60 min HNO₃-treated charcoal shows the maximum (i.e., 616 mV) and 1000° degassed having almost no oxygen shows the least (i.e., 322 mV) value of the half cell potential.

The results of the half cell potential values obtained on using KOH and methanol as electrolytes are also interesting. These values are higher than that of pure KOH, presumably, the surface oxygen complexes absorb methanol thus resulting in change of electrode potential. There is enough information available (Puri *et al* 1964; Kipling and Wright 1968; Puri and Bansal 1965). The CO₂-complex

References

- Kipling J J and Wright E H W 1968 *J. Chem. Soc.* p. 3382
Puri B R and Bansal R C 1965 *Carbon* **3** 227
Puri B R, Myer Y P and Sharma L R 1956 *J. Indian Chem. Soc.* **33** 781
Puri B R, Sandle N K and Sharma S K 1963 *Indian J. Chem.* p. 1418
Puri B R, Sandle N K and Talwar Chitranghda 1964 *J. Indian Chem. Soc.* **8** 58