

OXYGEN-REDUCING POROUS CARBON ELECTRODE FOR ELECTROCHEMICAL POWER SOURCES WITH ALKALINE ELECTROLYTES

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Summary

The performance of electrodes made from coconut-shell charcoal in alkaline fuel cells and metal/air batteries is reported. The electrode can be loaded with practically acceptable current densities of 500 - 2000 A/m² without deterioration for periods up to about 200 h. To achieve this performance, optimization of electrode structure was found to be necessary. Several chemical and physical techniques were employed to this end. Results show that coconut-shell charcoal is an excellent, low-cost substrate for porous carbon based air electrodes and further work may enhance its potentialities.

Introduction

Electrochemical power systems such as fuel/air fuel cells and metal/air batteries contain carbon electrodes that are oxygen-reducing cathodes. These devices can employ alkaline electrolytes which, in addition to their high conductivity and lower corrosivity, offer the possibility of using carbon electrodes without any additional catalyst. However, owing to the limited solubility of oxygen in alkaline electrolytes, the reduction of oxygen cannot be performed on smooth carbon electrodes at sufficiently high current densities and, hence, carbon electrodes with porous structures are employed. Various types of active carbons have been documented [1 - 9] as suitable substrate materials for oxygen-reducing electrodes. Coconut-shell charcoal has been employed as a substrate for fabricating air electrodes in air-depolarized cells [7 - 9], but the current densities of 50 A/m² on continuous loading and 250 A/m² on intermittent loading for times not exceeding a few seconds are too low for use in fuel cells or secondary batteries. We have therefore carried out extensive investigations on the physical and chemical tailoring of the coconut-

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shell charcoal substrate for fabricating uncatalyzed porous carbon electrodes for the efficient electro-reduction of oxygen in alkaline cells. After carrying out detailed optimization studies, we have concluded that the oxygen-reducing electrodes described here could be loaded with acceptable current densities without deterioration for practical periods of operation.

Experimental

(i) Preparation of active carbon

Active coconut-shell charcoal obtained from Talaulicar Carbons, India, was subjected to repeated gravity separation with saturated calcium chloride solution to remove the denser ingredients, if any. The charcoal thus obtained was subjected to repeated 'soxhlet' treatment with azeotropic hydrochloric acid in order to remove any inorganic impurities present. It was next washed with distilled water in the soxhlet itself to remove the chloride content and then dried at about 150 °C in a vacuum oven. The ash content of this charcoal specimen was found to be about 0.03%, which is lower than the ash content values of 1.5% - 6% reported for the other carbons [1 - 6].

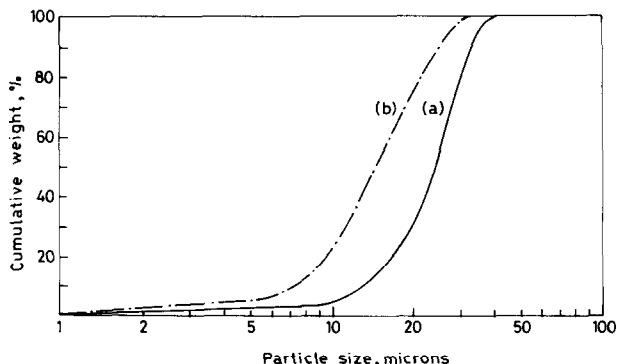


Fig. 1. Particle-size distribution curves for: (a) unactivated 400 mesh sieved charcoal, density 1.77 g/cm³; (b) gas-activated 400 mesh sieved charcoal with 66% weight loss, density 1.59 g/cm³.

The prepared charcoal was subjected to mechanical grinding and sieving through a 400 mesh sieve. The particle-size distribution of the sieved charcoal obtained using the sedimentation method is shown in Fig. 1(a). It can be seen that the majority of the particles lies in the 10 - 30 μm size range.

'Gas activation' of the sieved carbon was achieved by heat treatment in a carbon dioxide atmosphere at 900 °C for 4 - 5 h, followed by heating at the same temperature for 4 - 5 h in an ammonia atmosphere with the gas flow rate maintained at 2 - 4 l/h between the initial rise and final decrease in temperature. Gas activation of the carbon substrate was preferred rather than further grinding because studies by Tantram and Tseung [10] and Mrha [11]

showed that unlike carbons subjected to grinding, the carbon particles in gas-treated specimens did not agglomerate. Gas activation resulted in a loss in weight of the carbon substrate, the extent of which varied with the duration of the activation procedure. Carbon substrates with weight losses ranging between 47 and 66% were prepared. The density and the particle-size distribution of the carbon substrate were also found to decrease substantially on gas activation.

The particle-size distribution for a gas-activated charcoal specimen with 66% weight loss is shown in Fig. 1(b); this distribution curve shows that the majority of the carbon particles are within the range 5 - 20 μm . The density of this carbon substrate was found to be 1.59 g/cm^3 as against 1.77 g/cm^3 for the unactivated carbon.

(ii) Preparation of porous carbon electrodes

Electrodes of various carbon specimens were prepared by hot pressing the carbon substrate on expanded platinum metal (Exmet) screens (0.06 mm dia. wire, 1024 mesh/ cm^2) with polyethylene powder (average particle size $\sim 5 \mu\text{m}$) as binder. The die assembly containing the mixture of carbon and polyethylene was heated at $\sim 140^\circ\text{C}$ by a heater attached to its platten. The desired compaction load was applied over the die plunger at this stage. The load was sustained until the temperature of the die came down to $\sim 90^\circ\text{C}$ on cooling. Optimization of the binder composition and compaction pressure was achieved by testing the electrochemical performance of the electrodes (see below).

(iii) Measurements of physical parameters of porous carbon electrodes

Surface areas of the electrodes determined by the BET method ranged between 300 and 600 m^2/g depending on the nature of the carbon substrate, compaction pressure, and binder composition. The electrodes were examined by scanning electron microscopy, and micrographs of electrodes fabricated with gas activated and unactivated carbons are shown in Figs. 2 and 3. Micrographic information regarding the intra- and inter-pore structure of the

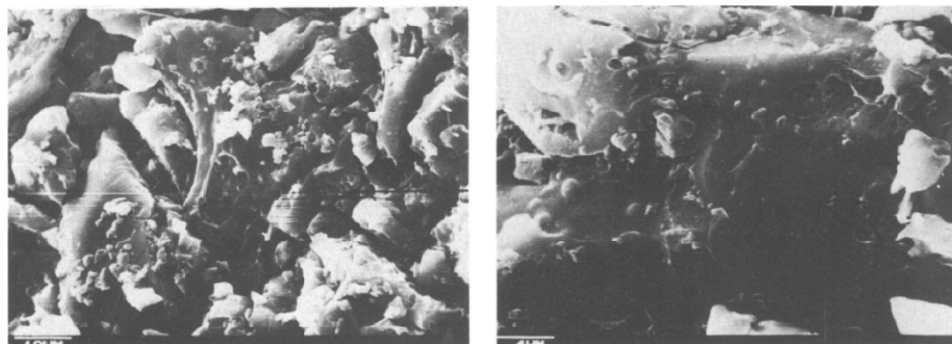


Fig. 2. Electron micrographs of unactivated carbon electrodes: (a) inter-pore structure; (b) intra-pore structure.

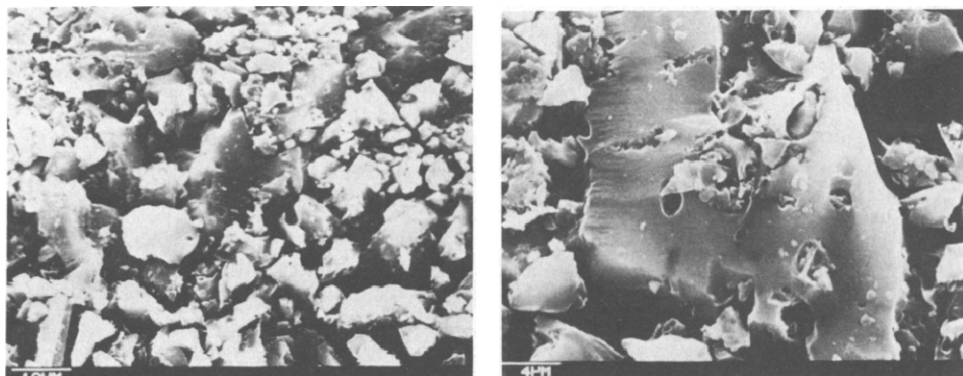


Fig. 3. Electron micrographs of gas-activated carbon electrodes: (a) inter-pore structure; (b) intra-pore structure.

bonding carbon substrate assisted in optimizing the electrode structure. Examination of the micrographs shown in Figs. 2 and 3 indicates that gas activation makes the inter-pore structure in the electrodes uniformly heterogeneous* (see Figs. 2(a) and 3(a)), which is a desired feature for carbon gas-diffusion electrodes. However, as seen from Figs. 2(b) and 3(b), no substantial change seems to occur in the intra-pore structure. The resistivities of the electrodes were ~ 0.4 ohm cm.

(iv) Characterization of carbon substrates using X-ray photoelectron spectroscopy

The core level spectra of various carbon substrates (both untreated and treated with gases) were examined by X-ray photoelectron spectroscopy. The C(1s) spectra for various samples are shown in Fig. 4. It can be seen that there is no significant change in the binding energies and line-shapes for differently treated samples. This would imply that the bulk of the carbon sample remains in the same chemical state before and after the gas treatment. A weak, broad signal was found for the N(1s) level of the sample treated with NH_3 (see Fig. 5(a)); there are more than one species of N(1s) on the surface of the sample treated with CO_2 and NH_3 , as indicated by more than one N(1s) peak (see Fig. 5(b)). The relative contributions of these species, however, appear to vary with gas treatment of the samples.

(v) Measurements of the electrochemical performance of oxygen-reducing electrodes

The electrochemical cell designed to measure electrochemical performance parameters contained the porous carbon working electrode, an Hg/HgO, OH^- reference electrode equipped with a Luggin capillary, a high surface area flat-bed counter electrode made from sintered nickel, a magnetic

*The term signifies that the pore-size distribution is visibly uniform all over the electrode surface.

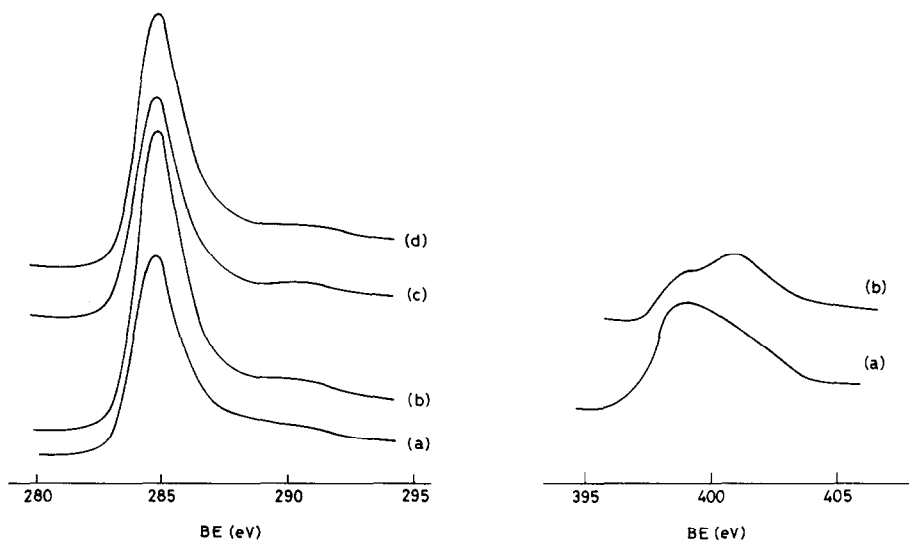


Fig. 4. X-ray photoelectron spectra of C(1s) region of various carbon substrates: (a) untreated carbon; (b) CO₂-treated carbon; (c) NH₃-treated carbon; (d) CO₂- and NH₃-treated carbon.

Fig. 5. X-ray photoelectron spectra of N(1s) region of carbon substrates treated with: (a) NH₃; (b) CO₂ and NH₃.

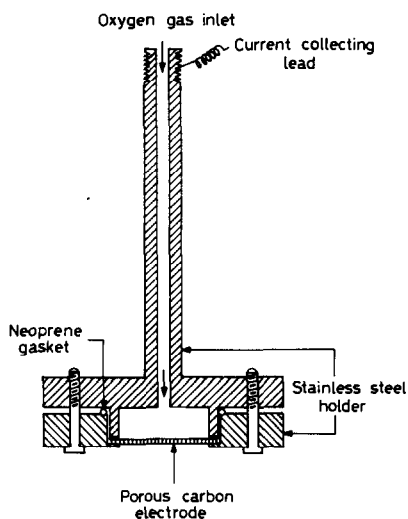


Fig. 6. Electrode holder assembly.

stirrer submerged in the electrolyte (which was either 1M KOH or 6M KOH solution in double distilled water), a bimetal, power-regulated heater, and a thermometer. The electrode holder (Fig. 6) had a gas chamber on the rear side of the working electrode. This was sealed by arranging for the current-collecting metal block to press tightly against the electrode.

Galvanostatic polarization studies were carried out with a regulated d.c. power supply and a high-power-rated rheostat in series with the electrochemical cell. Current-potential curves for cathodic reduction of oxygen (medical grade) were obtained for the electrodes described here. The effects of changing the composition of the binder, compaction load, and carbon substrates on the electrochemical performance of the electrodes at room temperature in 1M KOH were studied first. After the initial screening of electrodes, further electrochemical performance tests were conducted in 6M (27% w/v) KOH at both 30 and 60 °C. The influence of the oxygen gas pressure upon the electrochemical performance of the electrodes was also examined.

Results and discussion

Initial tests showed that a compaction pressure of 0.05 ton/cm² and a binder composition of 20 wt.% were optimum for electrodes of either type of carbon substrate. The electrochemical data for various types of electrodes are summarized in Table 1. It is noteworthy that several physico-chemical measurements were carried out to ascertain the optimum binder composition, pressing load, compaction temperature, and also the reproducible behaviour of the electrodes. The electrochemical performance of the electrodes compacted with the carbon substrate of 66 wt.% loss was found to be the best. This could be attributed to factors such as increased electrode surface area, formation of defined inter-pore structure, and increased surface activity of the carbon substrate by the formation of catalytically active nitrogen groups, as suggested by Mrha [1]. Electron spectroscopic studies on catalytic carbon electrodes are being conducted at present in this laboratory to examine the nature of such nitrogen groups and also to discover the cause of their electrochemical reactivity. Since there is no significant change in the binding energies and the line shapes of C(1s) X-ray photoelectron spectra of differently

TABLE 1

Electrochemical data from preliminary screening of oxygen-reducing porous carbon electrodes with oxygen gas pressure at 90 mmHg

Electrode type	Loss of carbon on gas activation (wt.%)	KOH concentration (M)	Cell temperature (°C)	Compaction pressure (ton/cm ²)	Observed potentials vs. Hg/HgO, OH ⁻ at load current density of 1000 A/m ² (V)
1	57	1	30	0.064	-0.235
2	66	1	30	0.064	-0.235
3	66	1	30	0.05	-0.200
4	66	6	30	0.05	-0.125
5	66	6	60	0.05	-0.105

treated carbon specimens, speculation of change in the chemical structure and environment of the bulk carbon on gas activation can be discounted (see Fig. 4).

The current-potential curves for the cathodic reduction of oxygen on the above electrodes are shown in Fig. 7; the curves are not corrected for IR losses. Figure 7 also includes the data of Horowitz *et al.* [3] for a 10% Pt/RB-

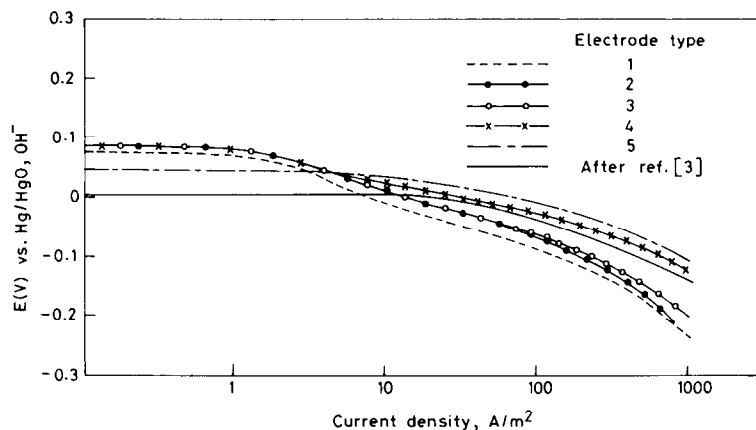


Fig. 7. Performance curves obtained for oxygen reduction in 1M and 6M KOH on electrodes of types 1 - 3 and types 4 and 5, respectively. Performance curve for a 10% Pt/RB-carbon catalyzed electrode at 75 °C in 3M KOH electrolyte (ref. 3) also shown for comparison.

carbon catalyzed electrode at 75 °C in 3M KOH. The electrochemical performance of type-5 electrodes (Table 1) of the present study, which do not contain a catalyst, is clearly superior to that found by Horowitz *et al.* for a Pt-catalyzed porous carbon electrode.

Current-potential curves for type-4 electrodes over a range of oxygen gas pressures (50 - 130 mmHg) are shown in Fig. 8. The data clearly show

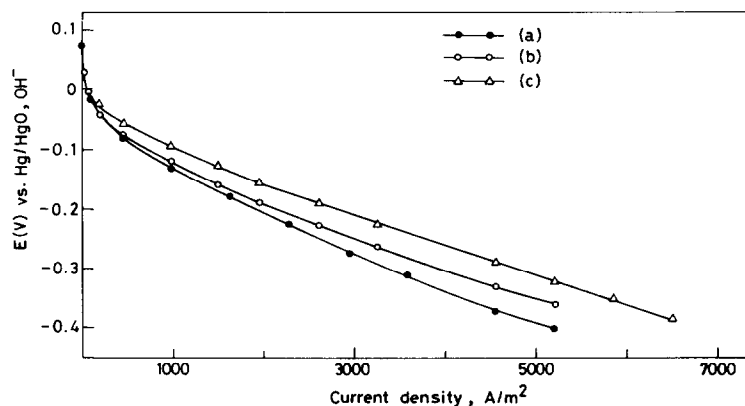


Fig. 8. Current-potential curves for type-4 electrodes at oxygen gas pressures: (a) 50, (b) 90, (c) 130 mmHg.

that mass polarization has been averted sufficiently for the electrodes to be loaded at high current densities. The polarization curves are practically rectilinear in the current density ranges of this study. This clearly demonstrates that the rate of the electrode reaction is not controlled at any current density by irreversible charge-transfer processes. Comparison of the current-potential curves indicates that on changing the oxygen gas pressure from 50 to 130 mmHg, there is a decrease in electrode polarization from a few mV at open-circuit to ~ 100 mV under heavy load. The effect of temperature was, however, small (see Table 1).

Tests were also conducted using type-4 electrodes with load current densities ranging from 500 to 2000 A/m² for periods of several hours. The operational curves are shown in Fig. 9. No deterioration was seen over the period of the tests. It was only at an appreciably high current density of 5200 A/m² that the electrodes started to deteriorate slowly after about 2 h. Exhaustive service life tests are in progress at present. Such performance is encouraging and is far superior to any other reported for carbon-based air electrodes.

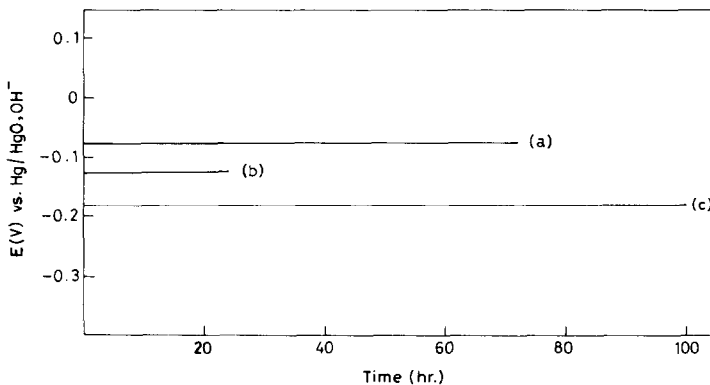


Fig. 9. Operational curves for type-4 electrodes driven at load current densities: (a) 500 A/m²; (b) 1000 A/m² after 500 A/m² for 72 h; (c) 2000 A/m² after 500 A/m² for 72 h and later 1000 A/m² for 24 h. Room temperature (~ 30 °C) with oxygen gas pressure maintained at 90 mmHg.

Further improvements could possibly be obtained by depositing suitable surface catalysts on to the above electrodes, and by controlling the structure of the hydrophobic binder and catalyst to achieve an improved three-phase (gas/liquid/solid) interface. Research and development work in these directions is to be taken up in collaboration with the University of Oxford, U.K.

Conclusion

The present study has resulted in the development of a method of fabricating porous carbon based air electrodes from coconut-shell charcoal which

can carry acceptable load current densities without deterioration. The preparation is simple and the performance is competitive with other carbon electrodes reported in the literature. Further development work on this electrode substrate may give rise to even better ranges of performance.

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