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# POROUS CARBON ELECTRODES FOR NON-MERCURY CHLOR-ALKALI CELLS

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## SUMMARY

Porous carbon electrodes were prepared using carbon powders of different types using various catalysts. Physical properties of the prepared electrodes were evaluated using scanning electron microscopy (SEM), surface area analyser etc. Performance characteristics of these electrodes were evaluated by galvanostatic polarisation at various temperatures in 6M potassium and sodium hydroxide solutions.

## INTRODUCTION

Chlorine and caustic are almost entirely produced by electrochemical means. Caught between high energy cost and low product prices, chlor-alkali producers world-wide are now turning towards membrane cell technology for survival. Membrane based technologies have improved so much in recent years. One development is the oxygen depolarizing cathode process. In this process, an alternate cathodic reaction, that is, the reduction of oxygen rather than the conventional decomposition of water, is used for producing caustic [1].

Electrochemical power sources such as metal/air batteries and fuel cells contain carbon electrodes for oxygen

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*Portugaliæ Electrochimica Acta, 10 (1992) 39-48*

reduction. Coconut shell charcoal has been empolyed as a substrate for fabricating air electrodes in air depolarized cells [2-4]. Teflon bonded multilayer carbon electrodes have been developed [5,6]. Materials selection and pretreatment is given prime importance [7-9]. The electrode baking should have high permeability to gases, structural strength, corrosion resistance and high conductivity [10]. The electrochemical properties of air-solution-carbon electrodes depend not only on the kind, contents of the electroactive material, interal surface area or the particle size of the components, but also on the preparation conditions for example, an increase in the temperature of sintering of teflon-bonded electrodes was found to result in a decrease of the electrical resistance of the electrodes, and simultaneously in a rise of the current density of oxygen reduction [11,12].

Hence, investigations were carried out on the chemical and physical tailoring of the activated charcoal substrate for fabricating porous carbon electrodes used in chlor-alkali cells.

## EXPERIMENTAL

### Preparation of Porous Carbon Electrode

Activated charcoal available from S.D.Fine chemicals., was used as such without further treatment. Acetylene black was used as hydrophobic material. Catalization was done by chemical reduction method as well as thermal decomposition method.

The required amount of carbon powder, filler material and polytetrafluoroethylene (PTFE) emulsion was mixed well by

mechanical stirrer. The whole mixture was filtered, washed with distilled water and dried in air oven at about 370-380$^{\circ}$K. Then, the mixture was pulverized. Double layer electrodes were prepared. The layer facing the electrolyte (working layer) alone contained the catalyst. The mixture of required amount of carbon powders was pelletized at room temperature at a pressure of 300 kg/cm$^2$, followed by hot pressing at 620-630$^{\circ}$K. All the electrodes had nickel(Ni) mesh as current collector.

### Evaluation of Physical Parameters

The particle size of carbon powders (both catalyzed and un-catalyzed) were determined using a particle size analyzer. The surface area of the powders was analyzed using a surface area analyzer at liquid air temperature. The porosity of the electrode samples were analyzed using mercury penetration porosimeter. The morphology of the internal structure of the electrodes were analyzed using SEM.

### Electrochemical Behaviour

The prepared electrodes were subjected to steady state galvanostatic polarization using a conventional H-type electrochemical cell fabricated using polypropylene. Porous nickel as counter electrode and Hg/HgO, OH$^-$ as reference electrode were used. Electrodes were polarized at room temperature as well as at 333$^{\circ}$K. Polarization studies were conducted in 6M potassium (KOH) and sodium hydroxide (NaOH) solutions. Oxygen gas flow and pressure were measured by manometers.

## RESULTS AND DISCUSSION

Various types of double layer electrodes, both catalyzed and un-catalyzed, were prepared. The electrodes were catalyzed only in the layer facing the electrolyte. The gas diffusion layer of all the electrodes were similar, and the same amount of binder (PTFE) was used in the preparation of all the electrodes. Other preparation conditions such as temperature, compacting pressure etc., were also maintained the same. Catalyst loading and porosity of different electrodes are presented in Table I. There is only a marginal difference (60 to 65%) in the porosity of these electrodes.

**Table I** : Amount of Catalyst and Porosity of Different Type of Electrodes

| Electrode Number | Type of Electrode | Catalyst Amount ($mg/cm^2$) | Porosity (%) |
|---|---|---|---|
| 1 | Un-catalyzed | -- | 63.4 |
| 2 | Ni-catalyzed | 10 | 62.5 |
| 3 | Ni-catalyzed | 15 | 62.1 |
| 4 | Ru-catalyzed | 5 | 64.8 |
| 5 | Ru-catalyzed | 8 | 64.6 |
| 6 | Pt-catalyzed | 1 | 65.0 |
| 7 | Pt-catalyzed | 2 | 65.2 |
| 8 | Pt-catalyzed | 3 | 65.5 |

However, porosity decreases slightly in the case of Ni-catalyzed electrodes. By observing the gas flow rate and gas over-pressure

on the electrodes using manometers, it was found that the electrodes catalyzed with platinum had good gas diffusion characteristics in comparison with those catalyzed with either Ni or ruthenium (Ru). The porous character of the electrodes may be increased by using activated charcoal of high quality.

The specific surface area of the powders were analysed using BET method and are reported in Table II. The powder in the working layer of the electrode and (which is the best electrode) has high surface area compared with Ni-catalyzed powders.

**Table II** : Specific Surface Area ($m^2$/cc) of Various Carbon Powders Used in the Preparation of Electrodes

| Electrode No. | Layer | Specific Surface Area |
|---|---|---|
| 1 | Gas Layer | 0.080 |
| 1 | Working Layer | 0.180 |
| 2 | Working Layer | 0.034 |
| 3 | Working Layer | 0.860 |
| 4 | Working Layer | 0.046 |
| 5 | Working Layer | 0.048 |
| 6 | Working Layer | 0.050 |
| 7 | Working Layer | 0.054 |
| 8 | Working Layer | 0.060 |

The electrode thickness was found to be in the range of 1.35 to 1.45 x $10^{-3}$m.

The morphology of the electrode samples were analysed using SEM. The morphology of the gas diffusion layer (common for all the electrodes) is shown in Fig.1. Similarly the working layer of electrodes 1,6 and 8 are shown in Fig.2,3 and 4 respectively. Fig.4 clearly shows that platinum (Pt) is dispersed uniformly in the electrode. This can be compared with the morphology of the working layer of uncatalyzed electrode in Fig.2. The morphology of the working layer of the electrodes which contain different amounts of platinum are presented in Fig.3 and 4 and shows similar morphology. SEM analysis of the working layer of electrodes 2,3,4,5 and 7 were found to have similar characteristics.

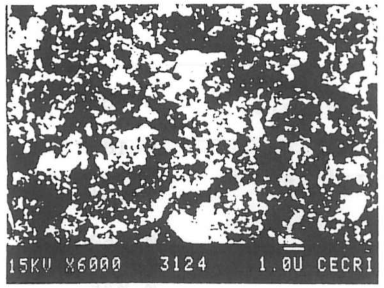

**Fig.1.**SEM micrograph of the gas diffusing layer

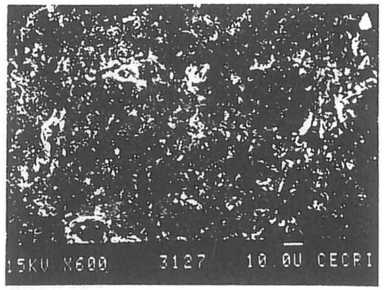

**Fig.2.**SEM micrograph of the working layer of Electrode No.1

The electrochemical behaviour of all the electrodes were studied by steady state galvanostatic technique. The polarisation was done at various temperatures in potassium and sodium hydroxide solutions. The polarisation behaviour of electrodes 1,2,4,6 and 8 in 6M KOH at 333$^{o}$K is shown in Fig.5. The

performance of the electrode [13] is also shown for comparison. During polarisation, the oxygen gas over pressure was maintained at 30 - 40 mm mercury (Hg).

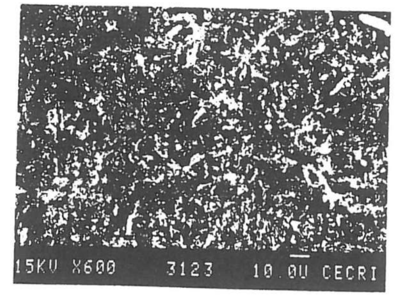

**Fig.3.**SEM micrograph of the working layer of Electrode No.6

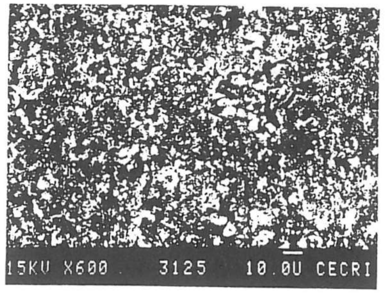

**Fig.4.**SEM micrograph of the working layer of Electrode No.8

From Fig.5, the un-catalyzed electrode (No.1) is found to have poor performance while the electrode No.8 which contained maximum amount of platinum, showed very good performance. The polarisation curves are almost rectilinear indicating that the

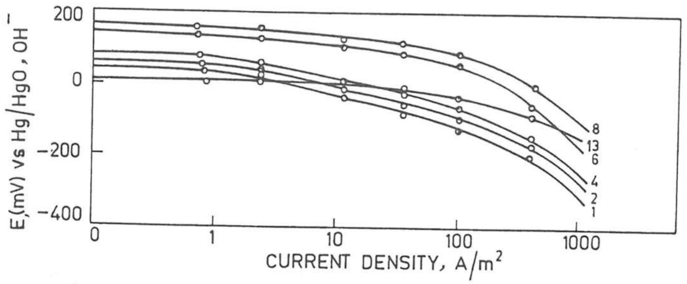

**Fig.5.**Galvanostatic polarisation in 6M KOH solution

rate of electrode reaction is not controlled by irreversible charge transfer process. The influence of oxygen gas over - pressure on the electrode within the range 30 - 40 mm Hg is not substantial.

Polarisation studies in 6M KOH at room temperature showed similar behaviour. The open circuit potential (OCV) of all the electrodes (Table III) is very low in the case of uncatalyzed electrode and very high in the case of electrode No.8. The OCV of the electrodes increases with increase in electrode performance, during polarisation. The steady state galvanostatic polarisation of all the electrodes were studied in NaOH solution both with respect to concentration and temperature (Fig.6).

**Table III** : Open Circuit Potential (mV) of Different Electrodes in 6M KOH and 6M NaOH Solutions at 333°K

| Electrode Number | Open Circuit Potential vs Hg/HgO, $OH^-$ | |
|---|---|---|
| | 6M KOH | 6M NaOH |
| 1 | + 0.047 | + 0.040 |
| 2 | + 0.052 | + 0.047 |
| 3 | + 0.058 | + 0.051 |
| 4 | + 0.060 | + 0.053 |
| 5 | + 0.064 | + 0.058 |
| 6 | + 0.115 | + 0.103 |
| 7 | + 0.147 | + 0.137 |
| 8 | + 0.160 | + 0.150 |

The electrochemical behaviour of all the electrodes

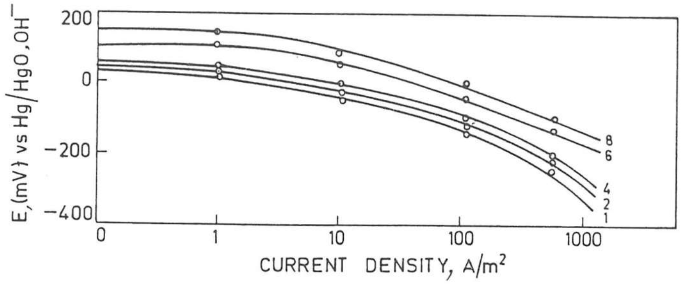

**Fig.6.**Galvanostatic polarisation in 6M NaOH solution

(Table III) are low in NaOH as compared to KOH solutions. However, the order of performance remains the same and showed high stability ( > 48 hours).

## CONCLUSION

It may therefore be concluded that the performance of gas diffusion electrodes could be enhanced by the incorporation of platinum as catalyst and also by the use of carbon powders having large surface area and low particle size. Further improvements could be achieved by using the carbon powder of good quality and by using various catalysts like porphorin, pthalocyanine etc.

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(Received, 3 February 1992)
(Revised form, 23 July 1992)

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# NON-LINEARITY OF CALIBRATIONS IN THE ANALYSIS OF ANIONS BY ION-CHROMATOGRAPHY WITH SUPRESSED CONDUCTIVITY DETECTION

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## ABSTRACT

Non-linearity of calibration in the determination of anions by ion-chromatography with supressed conductivity detection is re-examined. With a carbonate eluent, the curvature is demonstrated for $NO_3^-$, $Br^-$ and $SO_4^{2-}$ calibrations using plots of the logarithm of the normalized peak area against the logarithm of the anion concentration. These graphs were also evaluated theoretically assuming the peak shape is Gaussian. It is demonstrated that for sufficiently low concentrations linear calibrations are obtained and that deviations are to be found in the middle of the concentration range. Several procedures are discussed to avoid having large errors in analysing samples over a wide range of concentrations.

## INTRODUCTION

The term "ion-chromatography", introduced by Small et al in 1975 [1], originally was used to describe a system of ion-exchange chromatography using a low capacity ion-exchange column, a suppressor column and a conductivity detector. More recently, the definition has been broadened so that "ion-chromatography" is now generally applied to any modern chromatographic method for determining inorganic and organic ions. The word "modern" implies that the separation is high performance (or rapid) and that automatic detection is employed.

Suppressed anion and cation chromatography employ post-column chemistry to reduce the background signal and allow conductometric detection of sample ions [2]. Ion determinations by single column ion-chromatography are performed with the separation column connected directly to the detector [3].

Ion chromatography is a useful and sensitive method for the determination of ions, specially for inorganic anions and has found widespread application. When a