Preparation and characterisation of porous electrodes from nickel powder for fuel cells

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Porous gas diffusion electrodes are used in fuel cells. The essential requirement of the porous electrodes is to establish an internal gas/liquid interface as long as the current is drawn from the cells. INCO nickel-255 powder is used for making porous electrodes by powder compaction and sintering techniques. The porosity and pore-size distribution in the electrodes are correlated with the compaction pressure, sintering temperature, amount of pore formers and particle sizes of catalysts. A method for the fabrication of two layer and three layer electrodes with graded porosity is outlined.

Metal powders of nickel, iron especially carbonyl variety have been widely used in battery industry. INCO nickel-255 and 287 have been employed for the fabrication of electrodes in alkaline nickel-cadmium, nickel-iron and nickel-zinc batteries and in fuel cells. The high compressibility of these metal powders during compaction associated with good mechanical strength during sintering is the essential criteria for the long-term stability of these battery electrodes.

In fuel cells, especially in low temperature hydrogen-oxygen fuel cells, which operate with aqueous KOH as electrolyte at 60-80°C, the electrodes are made up of INCO nickel-255 powder. The hydrogen or oxygen gas, which is supplied to the anode or cathode compartment is allowed to establish a contact with the KOH electrolyte within the porous electrode structure (Fig. 1). The generation of current is thus dependent upon the wetted area of the three-phase reaction zone. This requires a narrow pore size distribution of the electrode structure to avoid either complete flooding of the pores with the electrolyte or bubbling of gas through the pores. Hence, the establishment of mixed pores with macro, micro and interconnected pores is the choice. This can be easily achieved by proper control of the particle size of the nickel powders, catalysts, pore formers and the amount of pore formers. Usually the catalyst powders which essentially catalyse the electrochemical reactions (called electrocatalysts) are mixed with nickel powder (support) in the fabrication procedures.

More frequently, electrodes with graded porosity structure have been prepared. A double layer or triple layer structure is usually envisaged (Fig. 1). The layer exposed to the electrolyte consists of micro pores and is completely filled with electrolyte. This is called fine pore layer (FPL). The adjoining layer contains the catalysts and usually has slightly bigger (medium) pores, where the three-phase reaction zone exists. This layer is called the catalyst layer (CL) or medium pore layer. This layer is further supported with another layer containing macro pores called coarse pore layer (CPL). This is essentially a triple layer model. In certain cases, both CL and CPL are merged to form a single layer such that the electrode is essentially a double layer model.

This paper describes the fabrication procedures for making double layer and triple layer electrodes by powder compaction and sintering techniques. The effects of different amounts of pore-formers on the pore size distribution of the various layers are presented. The ratios of thickness of FPL to CL/CPL are varied with a view to achieve mechanically stable and highly performing porous gas diffusion electrodes.

Experimental Procedure

The INCO nickel-255 powder was treated in H₂ atmosphere at 200°C in order to reduce any surface oxides present. The method of pre-treatment has been reported earlier. Raney nickel powder obtained from commercial Ni₂Al₃ alloy powder by leaching out Al in NaOH solution and after washing and drying, was used as the electrocatalyst for the hydrogen anodes. Silver supported on activated carbon or silver obtained from the decomposition of silver salts was used as the electrocatalyst for the oxygen cathodes. These catalysts were mixed with nickel-255 powder
in various proportions in a SS ball mill to form the
catalyst layer. Pore formers such Na₂CO₃, KCl,
NH₄HCO₃ and naphthalene, powder were used in the
range of 5-20 percentage by weight in the above
mixture.

Single layer and multi layer electrodes of circular
type with 4.4 cm and 6.2 cm dia were fabricated by
compacting the respective layers in a suitable die
under hydraulic compression. Pure Ni-255 powder
formed the FPL and the above powder mixture
formed the CL, while CPL consisted of Ni-255 plus
pore former only. Compaction pressures in the range
2 tonnes.cm⁻² to 4 tonnes.cm⁻² were tried. The green
compact was extruded from the die and then sintered
in H₂-atmosphere in a furnace at temperatures in the
range 700-900°C. The sintering assembly is shown in
Fig. 2. Care is taken to remove NH₄HCO₃ or
naphthalene wherever used, below 150°C in the same
assembly prior to sintering. Furnace rise time was
about 4-6 hr; sintering time was varied from 30 min to
1 hr and the cooling time 8-12 hr. Commercial grade
99.9% compressed hydrogen gas was used throughout
the entire operation.

The thickness measurements were made with
Cambridge Instruments-screw gauge at various points
and the average thickness values are reported. A
liquid absorption technique was employed to
determine the overall volumetric porosity of the
electrode. Dioxan was employed as the absorption
liquid medium. The surface examination was carried
out using a JEOL Scanning Electron Microscope
(SEM). Micromeritics Mercury Penetration
Porosimeter (Model 910 Series) was employed to
determine the specific pore volume and pore size
distribution of the porous electrodes by the method
described earlier. The gas bubbling pressure i.e. the
pressure at which the gas passes through one side of
the electrode to the other side was determined. The
porosity, pore size distribution and the bubbling
pressure were correlated with the fabrication
procedures.

Results and Discussions

The pre-treatment of the nickel powder by the
method adopted is reported to yield an increase in the
surface area of the nickel powder (24.7m²g⁻¹). The
nickel powder INCO-255 has a bulk density of 0.50-
0.65 gm cm⁻³, with an average particles size 2.2-2.6
μm. The catalyst particle size of skeletal nickel
[Raney nickel] was 10-17μm. The catalyst layer was
made up of nickel and catalyst particles in 1:1 weight
ratio.

Use of different pore forming agents

The use of Na₂CO₃ and KCl as pore formers
requires boiling of the sintered compacts in hot water
repeatedly as recommended by Jong et al. in order
to get rid of them completely. It was observed that
chloride removal was found to be still incomplete as
evidenced by the precipitation of green NiCl₂ in the
 pores of the sintered samples. However, the porosity
values were of the same order for these electrodes as
in the cases when volatile pore formers like
NH₄HCO₃ or powdered naphthalene were used.
Difficulties such as agglomeration of the powder
mixture and atmospheric moisture absorption
resulting in layer separation of the green compact
were encountered when NH₄HCO₃ was used as pore
former. Use of naphthalene as pore former required
slow and controlled heating (below 50°C h⁻¹) up-to 120°C for its complete removal from the green compact. This is further assisted by flushing the sintering chamber with compressed air or nitrogen. Otherwise it resulted in incomplete removal of naphthalene, leading to the deposition of carbonaceous residues on the surface of the electrodes. If the heating rate was too high (above 100°C h⁻¹), deformations and cracks were observed on the surface. In view of the easy removal of the naphthalene pore former, which resulted in electrode for use immediately, this procedure was adopted in the fabrication of porous gas diffusion electrodes for fuel cells.¹⁰

**Effects of amount of pore formers on the porosity of the electrodes**

The thickness (mm·g⁻¹) and porosity (percentage by volume) of Ni - 255 powder compacts obtained under compaction pressure are tabulated in Table 1. Also the values obtained with different amounts of naphthalene [5,10,15 and 20 weight percentage] are also tabulated. It is seen that the increase of compaction pressure decreases the thickness as well as the porosity values. The use of pore formers increases the volume porosity and the increase is found to be uniform with increase in the amount of pore former. A nickel compact obtained at 2.5 tonnes/cm², having a porosity of 15.5% is the representative characteristic of FPL. Similarly, nickel – 255 powder with 20% pore former and 65.7% porosity is the representative characteristic of CPL. The catalyst layer consisting of nickel, catalyst and 10% pore former has 50% porosity.

**Double layer electrodes**

The FPL and CL thickness values, were mainly controlled by changing the amount of material (wt.) employed to form these layers. The thickness and porosity values measured for these layers made under different compaction pressures are tabulated in Table 2. Though widely varying ratios were possible, gas diffusion electrodes with sufficiently good strength were formed only when the thickness of the FPL was greater than half that of the CL. The overall porosity of the two layer and three layer electrodes is controlled by the composition of the layers and the compaction pressure. The SEM photographs show the cross section of the double-layer electrode (Fig. 3a), the surface topography of FPL (Fig. 3b), CL (Fig. 3c) and that of CPL (Fig. 3d). It can be seen that there is a wider distribution of smaller and bigger pores in the CL and the sizes of the pores are markedly different in the other two layers.

The bubbling pressure values as a function of compaction pressure and thickness of FPL obtained for these electrodes are shown in Fig. 4. It is noted that the bubbling pressure increases with the increase in the compaction pressure and as well as with the thickness of the FPL and reaches a maximum for electrodes thicker than 1 mm. The change in thickness of CL for the double layer electrode does not have any effect on the bubbling pressure. This is evident from the fact that the bubbling pressure values for a single layer (FPL) electrode with 1 mm thick and a two layer electrode with 1mm FPL are same [1.2 kg cm⁻² (gauge pressure) in water]. Since the bubbling pressure increases with highly viscous solutions, this
value is higher \(1.8 \text{ kg cm}^{-1}\) in 6.0 M KOH solution. The above alkaline solution is often employed as the electrolyte in fuel cells. The increase of bubbling pressure with increase in the compaction pressure can be attributed to the reduction of pore diameter at high compaction pressures. The determination of the bubbling pressure values is relevant to the fact that at gas pressures above these values, the pores will be free from the electrolyte and the establishment of three-phase reaction zone is not possible within the electrode structures. Conversely, at pressures below the bubbling pressure values, the pores will be partially filled with the electrolyte according to the following relationship,

\[
P = \frac{2\gamma \cos(\theta)}{r}
\]

where, \(P=\text{pressure in dynes cm}^{-2}\), \(\gamma=\text{interfacial tension of the electrolyte [85 dynes cm}^{-1}]\), \(\theta=\text{contact angle \([105^\circ - 110^\circ \text{ for Ni}]\) and } r = \text{pore radius.}

Hence, a decrease of the test pressure will shift the three-phase reaction zone towards the catalyst layer side. The thickness of FPL will also contribute to the above. The proper choice and identification is possible by observing the pore-size distribution curves.

**Mercury penetration porosimetric data**

The mercury penetration volume-pore diameter relationship of FPL, CL, CPL and double layer electrodes are shown in Fig. 5. The pore size distribution curves (i.e. the first order derivative of the curves of Fig. 5) are shown in Fig. 6. The mercury penetration porosimeter read out is processed to obtain the percentage of pores having a specified range of pore diameter, internal surface area and total surface area by the method described earlier. The
values are presented in Table 3. The steep rise in the pore volume for different electrodes indicates that greater percentage of pores is existing in that range of pore diameter. This is indicated as a sharp maximum in Fig. 8. For example for FPL, the maximum pores exist in the pore diameter of around 1 μm. When, a pore former is used, this maximum is shifted to above 10 μm values which indicates the size of the macro pores in CPL. For CL, the distribution of pores occurs around 2 - 4 μm [52%], but still about 25% of the pores are in the range below 2 μm and the rest are around 10 μm. This is a clear indication that both the macro pores and micro pores are well distributed in this layer, interconnected by medium size pores. This is really the reaction zone. When CL and CPL are same, the reaction layer is on the CL. The distribution of pores in CL is independent of the thickness of either CL or FPL, which is further confirmed from the SEM diagrams shown [Figs 3a-d].

Considering the values of 85 dynes cm⁻¹ as the surface tension of 6 M KOH, for a pore diameter of 1.0 μm size, the pressure of gas should be higher than...
the 25 psig [1.8 kg cm\(^{-2}\) gauge pressure] to keep the pores free from alkali. In other words, at pressures less than 1.8 kg cm\(^{-2}\), the pores will be flooded with the electrolyte. For a pore diameter of 3 \(\mu\)m size, a pressure of 116 psig [1.1 kg cm\(^{-2}\)] is needed to avoid flooding with the electrolyte. Since this range is obtained in CL to a greater extent, the catalyst distributed in CL is able to take part in the electrochemical reaction. Since the sizes of pores in CPL are greater than 10 \(\mu\)m, they are not flooded with the electrolyte at a pressure of 1.1 kg cm\(^{-2}\). They are completely filled with gas, which is supplied to the reaction zone in the CL. For the double layer electrodes, the catalyst in the surrounding of the macro pores do not contribute to the generation of current. Hence, to achieve maximum utilization of the electrocatalyst, the concept of making triple layer electrodes was used.

**Triple layer electrodes**

In the triple layer electrodes, the CPL acts as gas supplying layer and FPL as the electrolyte filled layer. The catalyst is distributed in the CL only, the thickness of which is same as FPL. The pore size and pore volume are greatly influenced by the particle size of the catalyst, ratios of amounts of Ni to catalyst, the optimum being around 1:1 by weight and the amount of pore former. The particle size of the catalyst is kept around 10-17 \(\mu\)m and the amount of pore former at 5-10 percentage by weight. The porosity and pore size distribution curves are also shown in Figs 5 and 6.
Table 3—Data from the mercury penetration porosimeter

<table>
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<tr>
<th>System</th>
<th>Compaction pressure (tons/cm²)</th>
<th>Percentage of pores in the pore dia range</th>
<th>Total poro vol (mL/g)</th>
<th>Total internal area (m²/g)</th>
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<td></td>
<td></td>
<td>&gt; 10 μm</td>
<td>1-7 μm</td>
<td>2-4 μm</td>
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<td>Ni-255 (FPL)</td>
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<td>70</td>
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<td>Ni-255 (FPL)</td>
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<td>5</td>
<td>16</td>
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<tr>
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<td>Ni + pore former 20%(CPL)</td>
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<td>Activated carbon powder</td>
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<td>Raney nickel powder</td>
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<tr>
<td>CL with 5%</td>
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<td>CL with 10%</td>
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<td>pore former</td>
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<tr>
<td>with active carbon catalyst</td>
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<tr>
<td>Triple layer electrode</td>
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<td>Triple layer electrode</td>
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<td>10</td>
<td>17</td>
<td>25</td>
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respectively. The electrochemical performance relating to the pore size distribution have been reported 11,12.

Conclusion
For the fuel cell electrodes establishment of a gas-liquid contact is the essential requirement. This is restricted to a particular thickness within the electrode by the formation of graded porosity, double layer and triple layer electrodes. The amount and particle size of the pore former affects the overall porosity. The pore size distribution is altered by the amount and particle size of the pore former, compaction pressure and sintering conditions. The determination of bubbling pressure is useful to obtain the normal working pressure of these porous gas diffusion electrodes in fuel cells.

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