PREPARATION AND CHARACTERIZATION OF ANODES AND CATHODES FOR MOLLEN CARBONATE FUEL CELLS

G PRABHU, C SOLAIYAN, S DHINNA DAVANAHAN, I ARULJI, S MUZHUMATHI, R CHANDRASEKARAN AND R PATTABIRAMAN

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

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Nickel powder (INCO 255) was used to prepare the electrodes. The anode was a porous nickel plate. Pure Ni and (Ni + 10% Cr) anodes were also fabricated. Several batches of electrodes were prepared by different techniques like loose power sintering (LPS), slurry casting (SC), tape casting (TC) etc. These electrodes were sintered in flowing hydrogen atmosphere at 1973 K (except in the case of Cr containing electrodes where it was 1173 K) for one hour. The cathode was mostly composed of porous nickel oxide plate. The nickel electrodes were usually got lithiated and oxidized inside the cell. The prelithiated nickel oxide powders were prepared by solid state reaction of nickel and Li₂CO₃ and characterized by XRD and cast in the form of tapes using a doctor blade assembly.

Keywords: Cathodes and anodes, molten carbonate fuel cells.

INTRODUCTION

The molten carbonate fuel cell (MCFC) represents an efficient device for the conversion of chemical energy into electrical energy[1,2]. The attractive feature of MCFC is that a wide variety of fuels such as hydrogen, hydrocarbons, carbon monoxide and their mixtures (gasified coal or reformed gas) can be used. Fig. 1 shows the state of art materials for the electrodes and electrolyte structures. A typical fuel cell assembly consists of a porous nickel anode containing chromium to provide strength and sintering resistance (fuel electrode) and a porous lithium doped nickel oxide cathode (oxidant electrode) separated by the molten alkali carbonate electrolyte (62 mol% Li₂CO₃ and 38 mol% K₂CO₃) contained within a porous ceramic lithium aluminate matrix.

The cell is operated at 923 K, hydrogen is oxidized at the anode and oxygen in reduced at the cathode as per the following equations.

Anode

\[ \text{H}_2 + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2 + 2e \]  

(1)

Cathode

\[ \text{CO} + \text{CO}_3^{2-} = 2\text{CO}_2 + 2e \]  

(2)

Fig. 1: Schematic representation of the "state-of-art" molten carbonate fuel cell (Ref 1)
\[ \frac{1}{2} \text{O}_2 + \text{CO}_2 + 2e^- = \text{CO}_3^{2-} \]  

(3)

The fuel gas is a humidified mixture of H₂ + CO and the oxidant is a mixture of O₂ + CO₂ which contain water vapour.

The electrode materials must meet the following general requirements:

- high electronic conductivity
- high electocatalytic activity
- thermodynamic stability
- chemical inertness -- moderate cost
- interconnected porosity
- ease of fabrication
- corrosion resistance in molten carbonate

Various materials have been evaluated for use as anodes and cathodes [7-9]. Efficient fuel cell operation requires that the electrodes must have sufficient electrolyte to maintain the electrode/electrolyte reactant gas interface necessary for the electrochemical reaction to occur. This requires a careful control of overall porosity and pore size distribution within the electrode structure [10-12]. The state of art specifications and the different electrode materials studied are given in Table I.

Various additives have also been reported in literature to stabilize the electrode structure and enhance the electocatalytic activity [13-29]. The function of the additives is to reduce the loss of porosity during sintering and develop creep resistant materials. The creep is referred to as the shrinkage in thickness and change of shape. The sintering resistance is increased by the additives which are usually metals, or oxides of metals.

In this paper the characteristics of the anodes and cathodes prepared from INCO Ni powder are described.

**EXPERIMENTAL**

Three types of Ni powders INCO 255, 287 and 123 were used. The metal powders were treated in hydrogen atmosphere as reported elsewhere [30]. The resulting powder was sieved through sieves and powders below 400 mesh were used to prepare the electrodes.

Similarly chromium powder was also treated. Ni + 10 wt% Cr mixtures were also prepared in a ball mill.

Porous electrodes were prepared by cold compaction at 190 MPa and loose powder spreading in graphite moulds. They were sintered in hydrogen atmosphere at 1123 K. The sintering temperature for Ni-Cr powders was 1173 K. The details of the sintering conditions are reported recently [31].

The slurry casting and tape casting procedures were also adopted to prepare thin green tape/sheets of nickel. The process involves preparation of a slurry of nickel powder in water (solvent) with polyvinyl alcohol (PVA) liquid as the binder and glycerol as the plasticizer. The slurry was mixed and cast over a glass plate using a doctor blade assembly. The entire process is described in the flow sheet (Fig. 2). The cast bodies were removed from the glass substrate after 12 h of curing and stored.

The thickness, shrinkage and density measurements were carried out. These green tapes were flexible in nature. They were sintered in hydrogen atmosphere in a programmable furnace controlled at a heating rate 1 K/min. The porosity values were determined by liquid absorption technique.

**RESULTS AND DISCUSSIONS**

The powder characteristics of the nickel powders after hydrogen treatments are shown in Table II and compared.

<p>| Table I: Typical characteristics of MCFC electrodes |
|----------------------------------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th><strong>Material</strong></th>
<th><strong>Anode</strong></th>
<th><strong>Cathode</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabiliser</td>
<td>Chromium</td>
<td>---</td>
</tr>
<tr>
<td>Reinforcement screen</td>
<td>Nickel</td>
<td>SS</td>
</tr>
<tr>
<td>Porosity (Vol%)</td>
<td>50-70</td>
<td>70-80</td>
</tr>
<tr>
<td>Mean pore dia (μm)</td>
<td>3-6</td>
<td>7-15</td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>0.1-1.0</td>
<td>0.1-0.50</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.5-1.5</td>
<td>0.5-0.75</td>
</tr>
<tr>
<td>Other additives or alternate materials</td>
<td>Cu[5], Co[14]</td>
<td>Al[17]</td>
</tr>
<tr>
<td></td>
<td>Zr[15], Mg[16]</td>
<td>Li₂MnO₃[37]</td>
</tr>
<tr>
<td></td>
<td>Cu-Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alloys[21,22]</td>
<td>Ni-Al</td>
</tr>
<tr>
<td></td>
<td>Ni-Al</td>
<td>Alloys[23]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb[26]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LiFeO₂[27]</td>
</tr>
<tr>
<td><strong>Fabrication techniques</strong></td>
<td>Hot pressing, sintering &amp; slurry casting</td>
<td>Hot pressing, hot rolling, plasma spraying &amp; tape casting</td>
</tr>
</tbody>
</table>

19
with the literature values [32]. The density values reported by us are the tap density values while the values reported in literature are loose powder or bulk (apparent) density values. It is reported in literature that the lower bulk density values of types 255 and 287 Ni powders result in sintered plates with higher porosities [33], making them as suitable candidates for battery applications.

The density values of the hydrogen treated powders are higher than the untreated powders indicating that the particles are in close contact after hydrogen treatment. The use of hydrogen treated nickel powders may result in lower porosity values for the sintered plates than when untreated powders were employed.

The characteristics of the nickel electrodes prepared by loose powder sintering method are indicated in Table III. The density values of the sintered plates are close to the closely packed powder density values. The sinter density values of treated powder packs are higher than the untreated powder packs. The porosity values obtained are lower than the porosity values reported in [32]. This is probably due to the difference in sintering conditions employed by us. Higher sintering temperatures result in lower porosity values. Increase of sintering time beyond 30 - 60 minutes may not have much influence on porosity. But both of them were reported to influence the strength of the sintered body [33]. Improved strength and conductivity accompany a decrease in porosity as a consequence of the increase in bond area formed between particles. These sintering conditions become vital in achieving optimum electrode porosity.

The porosity of the compacts made from type 123 powder was found to be less than those obtained from type 255 or 287 powders. Though the experimental values are lower than the literature values, the trend remains the same. It is reported that the more spherically shaped type 123 powder with a high bulk density results in a denser sintered plaque, with a smaller pore dia. This seems that this powder is more suitable for the anode plaque requirements of MCFC. While the relatively higher porosity values obtained with type 255 and 287 powders suggest that the sintered plaques formed from them will be suitable for the cathode specifications. Mixing of the two powders can further be utilized to control the pore microstructures within the desired range. Efforts are on in this direction.

Unlike the anode, the cathode requires electrodes with higher porosity and broader pore spectrum. Slurry casting method has been developed and reported using aqueous polyvinyl alcohol or methyl cellulose as binders [34,35]. A similar process has been adopted by us. The sintering conditions are determined by the TGA and DTA analysis of the green nickel tapes. A typical DTA/TGA curve of the green nickel tape is shown in Fig. 3. Initially, there is a steady weight loss up to 383 K indicating that water from the green tape is removed. On further heating, a secondary weight loss is noticed up to 643 K indicating the plasticizer and binder materials are removed. Nickel starts oxidizing at temperature

\[
\text{TABLE III: Characteristics of nickel electrodes prepared by loose powder sintering}
\]

<table>
<thead>
<tr>
<th>Ni type</th>
<th>Ni\textsubscript{255}</th>
<th>Ni\textsubscript{287}</th>
<th>Ni\textsubscript{123}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>UT T</td>
<td>UT T</td>
<td>UT T</td>
</tr>
<tr>
<td>(sintd) (g/cc)</td>
<td>1.661 2.876 1.463 1.848 3.435 3.525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>62.340 64.110 79.230 68.180 48.180 46.900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theoretical value [28]</td>
<td>90.000 ---- 86.000 ---- 60.000 ----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UT - Ni powder untreated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T - Ni powder after hydrogen pretreatment</td>
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</tbody>
</table>
above 673 K in air. This is useful in determining the temperature profile during the sintering stage.

Consequently the electrodes are sintered in H$_2$ atmosphere at a slow heating rate of 1 K/min, with intermittent soaking stages at 423 K for 3 h and 673 K for 3 h to remove the inorganic and organic constituents. The final sintering temperature is 1073 K for one hour and the product is cooled to room temperature at 1 K/min.

Table IV indicates the characteristics of green tapes and the sintered electrodes prepared from these tapes after controlled sintering. Both the shrinkage factor, density values of the green and sintered plaques and the final porosity values are reported. The density of the green compact depends upon the binder content (wt%), slurry composition, solvent (water) content, plasticizer amount and casting rates [35]. In this case also, both the green and sinter density values for the Ni electrodes from Ni-123 powder are higher than the tapes employing Ni-255 or Ni-287 powders. The porosity values from Ni-287 tapes are higher than tapes from Ni-123 powder making them more suitable as cathodes.

A number of methods have been reported to prepare lithiated nickel oxide cathodes [36-39]. The most widely adopted method is the in-cell lithiation technique, where a sintered Ni plaque is used as the cathode. At the operating temperature of the fuel cell i.e., at 923 K, the nickel is oxidised to NiO under in-cell conditions and the Li$_2$CO$_3$ from the electrolyte reacts with the NiO making it lithiated. Pre-lithiated nickel oxide powders were also used to prepare the electrodes by either loose powder sintering or tape casting methods. But these methods were found to result in lower porosity values. But the tapes prepared from pre-lithiated powder were used in the cell as green tapes and the electrodes were sintered under insitu condition. This had resulted in better performance of the cells than while employing presintered cathodes. The details of this process, conditions employed and advantages will be reported shortly.

**CONCLUSION**

The characteristics of the nickel electrodes prepared from three types of commercial Ni powders were compared. The sintered electrode from type 287 and 255 offer as choice for the cathodes, and type 123 powder or mixtures can be employed for the anode. Tape casting is a convenient method of making porous nickel electrodes.

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