

# *Inhibition of sintering in molten carbonate fuel cell anodes*

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Molten carbonate fuel cells operate at 600–700°C. At these high temperatures, high surface area nickel anodes lose their activity rapidly due to sintering. A study of the sintering kinetics of Ni, Ni–Ag and Ag powder revealed that when Ni and Ag particles are present in similar numbers, sintering is significantly inhibited. This is achieved by minimizing volume diffusion between adjacent particles—Ni and Ag have virtually no solid solubility at any temperature. Paste electrolyte cells using such electrodes gave 114 mA/cm<sup>2</sup> at 0.65 V on 80% H<sub>2</sub>/20% CO<sub>2</sub> fuel, compared to 80 mA/cm<sup>2</sup> at 0.65 V for a cell using sintered nickel anodes.

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## **Introduction**

The molten carbonate fuel cell is one of the fuel cell systems which can use reformed hydrocarbon fuels and relatively cheap materials of construction. Furthermore, since it is operated at 600–700°C, relatively cheap base metal or metal oxides, such as Ni or lithiated NiO can be used as the electrocatalysts instead of precious metals. However, the performance of such cells, even when using pure H<sub>2</sub> as fuel, is very much lower than low temperature fuel cells. Earlier work [1, 2] has shown that the slow rate of H<sub>2</sub> diffusion through the molten carbonate electrolyte is the main limiting factor. Takahashi [3] has shown that by using porous palladium anodes, which provide an alternative diffusion path for H<sub>2</sub> diffusion via the bulk of the palladium, very high performance could be achieved. However, apart from cost considerations, this approach is not promising since the electrode decays due to sintering. Thus, it is not practical to use higher surface area anodes to provide more thinly wetted area to speed up the rate of H<sub>2</sub> diffusion, unless sintering can be inhibited.

There are two main stages of sintering [4, 5]. The initial stage consists of rounding of rough particle surface by surface diffusion. The activation energy for this process is 2–3 times lower

than the activation energy required for volume diffusion, which is responsible for the final sintering stage, the growth of necks between particles, shrinkage and grain growth. Obviously, the possibility of inhibiting the initial stage of sintering is remote and the main concern should be the inhibition of grain growth. Since two particles coalesce together via a volume diffusion mechanism, it is obvious that a low diffusion rate would reduce the rate of grain growth.

In heterogeneous catalysts, sintering inhibitors are often based on high surface area refractory oxides, such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgO or ThO<sub>2</sub>. However, sintering inhibitors for electrocatalysts must be electrically conducting, corrosion resistant and should not form a non-conducting protective oxide film under operating conditions. These requirements restrict our choice to metals. Since Ni is invariably used as the anode catalyst, a review of the published data [6] on the interdiffusion coefficient of Ni and other metals at 600–700°C should provide us with a good criterion for selecting the most suitable sintering inhibitor.

For sintering inhibition to be effective, the interdiffusion coefficient between Ni and the sintering inhibitor must be lower than the self-diffusion coefficient of Ni. Though some of the refractory metals, such as W or Mo, satisfy the

above requirements, they do not seem to be as attractive as Ag. The interdiffusion coefficient of Ni–Ag has never been determined because Cesaris [7] showed that Ni and Ag have almost no solid solubility at any temperature. At 600°C, the solid solubility of Ni in Ag is only 0.026%. Ag has the additional advantage over the refractory metals in that it is corrosion resistant in molten  $\text{NaLiCO}_3$ , does not form a non-conducting protective metal oxide film and it also functions as an anode electrocatalyst [1]. Therefore, the sintering kinetics of the Ni–Ag was studied in some detail.

## Experimental

### Sintering studies

The sintering behaviour of the Ni–Ag system was assessed in two ways:

(a) densification of sintered Ni–Ag powder compacts;

(b) change in surface area of Ni–Ag compacts after sintering.

Grade 'B' Ni powder, obtained from Int. Nickel Ltd., was mixed in a mortar with –300 mesh silver powder, obtained from Johnson Matthey Ltd; the mixed metal powders were then pressed at 2 tsi in a 1 in. diameter steel die. After checking their 'as pressed' density, they were sintered in  $\text{H}_2$ . The degree of densification after sintering is a good guide to the effectiveness of Ag as a sintering inhibitor. A continuous flow, gas chromatography method [8] was used to measure the BET surface of the sintered Ni–Ag compacts, since the classical BET method based on volumetric or gravimetric measurements is not sensitive for measuring surface areas below  $1 \text{ m}^2/\text{g}$ . In addition, since it is necessary to know the average particle size of the starting material, the Coulter Counter [9] was used to measure the particle size distribution of the Ni and Ag powder.

### Electrochemical evaluation

The Ni–Ag powders were applied onto one side of a 4 mm thick, 11.2 cm diameter, hot-pressed paste electrolyte disc (63.5%  $\text{MgO}$ , 36.5%  $\text{NaLiCO}_3$ ). On the reverse side, Ag–ZnO

powders, previously pre-sintered at 750°C for 24 h, were used as the cathode catalysts. The use of pre-sintered Ag–ZnO powder ensures that the cathode catalyst will not change its performance during the electrochemical evaluation. The cell assembly has been described in detail elsewhere [1].

## Results and discussion

The results for a series of Ni–Ag compacts plotted as % theoretical density (Fig. 1) shows

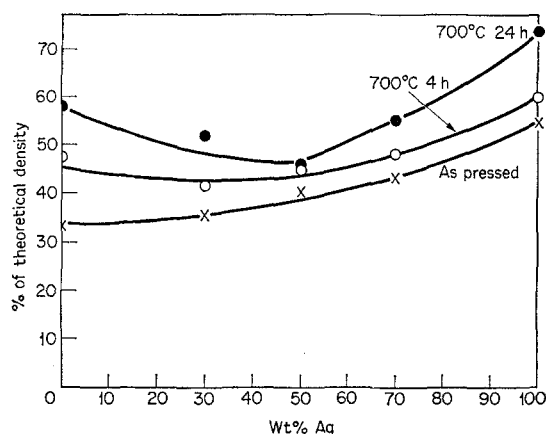


Fig. 1. The effect of Ag on the sintering of Ni.

that at Ni/Ag = 1, very little densification took place and densification virtually ceased after another 20 h at 700°C, confirming that addition of Ag greatly inhibited the sintering of Ni.

Surface area measurements showed that the Ni powder was  $0.58 \text{ m}^2/\text{g}$ , very much finer than the Ag powder ( $0.18 \text{ m}^2/\text{g}$ ). However, the average particle diameter of Ni and Ag, calculated from Coulter Counter results, indicated that they were in fact of similar size,  $3.75 \mu\text{m}$  for Ni and  $3.12 \mu\text{m}$  for Ag, suggesting that the Ni powder was very much rougher than the Ag powder and that they could be aggregated. Microscopic examination also showed that the Ni powders were rather rough and had a spiky appearance and that each individual grain consisted of several particles clustered together, whereas the silver particles were near spherical and had smooth surfaces. Fig. 2 shows the BET surface area of the sintered compacts, heated at 700°C for 24 h in  $\text{H}_2$ . This confirms that the highest surface area

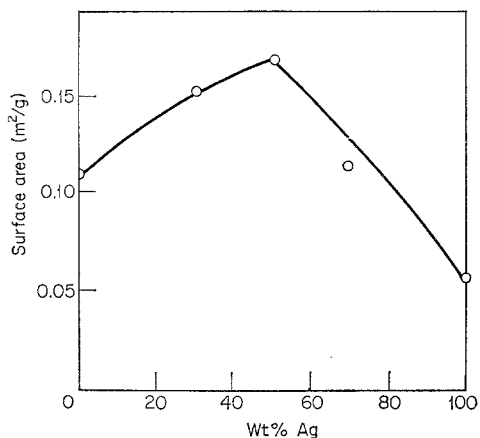


Fig. 2. Surface area of Ni—Ag compacts, sintered at 700°C for 24 h.

compacts have a Ni/Ag weight ratio of 1. This is equivalent to a particle ratio of about 1, confirming our earlier prediction that when Ni and Ag particles are mixed together, such that each Ni particle is in contact with an Ag particle and vice versa, sintering should be significantly inhibited. Fig. 3 shows the current voltage curves of a paste electrolyte cell using 50:50 Ni/Ag anode catalyst and a cell using porous nickel anodes. Though the performance is significantly improved, it is not directly proportional to the increased surface area of the anode catalyst. This

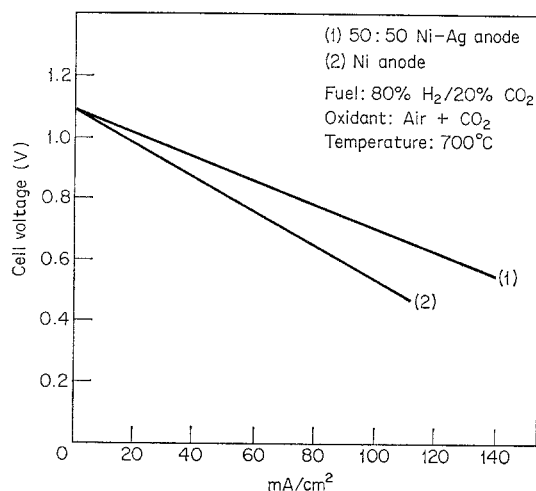


Fig. 3. Performance of Ni and Ni—Ag anodes.

is not surprising since Ag is known to be less active than Ni.

In principle, it is relatively easy to reduce the silver loading and still inhibit the sintering of the Ni anodes, provided the size of the added Ag powder is significantly less than that of the Ni powder. In practice, there is a practical limit to the allowable size reduction because the three phase interface in a paste electrolyte molten carbonate cell is maintained by the use of fine MgO fillers ( $<1 \mu\text{m}$  diameter) whose particle size is significantly smaller than the pores of the anodes or the cathodes. The use of fine MgO fillers ensures that the  $\text{NaLiCO}_3$  electrolyte would be kept inside the MgO pores by capillary forces. This approach should also be useful in medium temperature cells, high temperature solid oxide electrolyte cells and in other electrochemical systems where there is a need to stabilize the surface area of porous electrodes.

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