Short Communication

Void Volume Consideration in Evaluating the Capacity of Nickel–Cadmium Cells with Sintered Electrodes

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Summary

The cell capacity of a nickel–cadmium cell is proportional to the void volume and the loading level of active material in the pores. This work shows that, for conventional cell routine design procedures, these parameters are directly proportional to the sintered electrode thickness. The relations derived allow control of plaque thickness and weight in order to minimize fluctuations of sinter porosity and cell capacity in the course of production.

Sintering of raw plaques

The raw plaques for sintered-plate, nickel–cadmium cell electrodes are made from a substrate of perforated steel or screen, coated on both sides with dendritic nickel powder [1 - 3]. The powder can be applied dry in a mold, or wet in an aqueous slurry, and sintering takes place at a temperature of 850 °C - 1050 °C in an inert or reducing atmosphere. Under these conditions the powder particles are welded together and the result is a spongy structure, 0.5 - 1.5 mm thick, having a pore (void) volume between 80 and 85% of the apparent volume. The porosity of the electrode following the sintering process depends on many variables such as the properties of the powder, the sintering temperature, the time, and the atmosphere. Normally, to achieve a required porosity, a trial and error procedure is used. In this procedure the weights and dimensions of the electrodes are measured, and the porosities and void volumes are calculated. As a first trial condition for the sintering process, Fig. 1, which has been copied from ref. 4, is often used. This Figure depicts the resulting electrode porosity when INCO powder is used at various sintering temperatures. Following sintering, the raw plaques undergo an impregnation process in order to load the active material into the pores of the sinter. Prior to impregnation, however, the edges of the electrode areas are pressed (coined) to a thickness of 40 - 70% of the general plaque thickness. This increases the mechanical strength and

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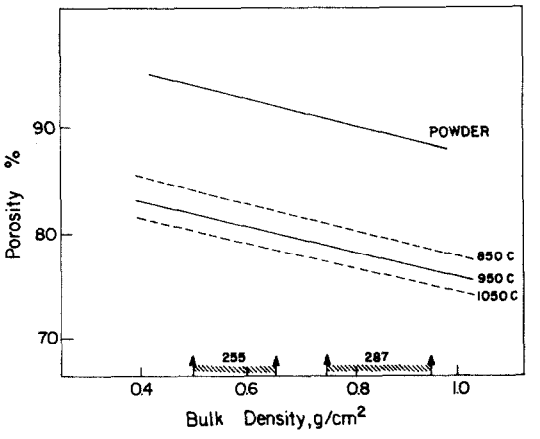

Fig. 1. Porosity of nickel powders 255 and 287 at various sintering temperatures.

minimizes sinter flaking, but slightly reduces the volume available for impregnation [5].

Capacity calculations

To control both the sintering and impregnation processes, it is necessary to derive the relationship between the sinter thickness, the raw plaque weight, and the pore volume in the plaque. These factors can be calculated from the non-pressed (active) area of the electrode (thickness, T_a; area, S_a), the pressed area (thickness, T_p; area, S_p), the corresponding area of substrate (thickness, T_s) and the total plaque area, S, in the following way:
The weight of the active area in a plaque is given by:

$$W_{a,p} = pS_{a,p}[D_n(1-P)(T_{a,p} - G/D_i) + G] \quad (1)$$

where the subscripts "a" and "p" are for the active and pressed parts, respectively.

Since the weights per unit area of both active and pressed parts are equal, the porosity of the pressed area in the plaque can be calculated by:

$$\frac{W_a}{pS_a} = \frac{W_p}{pS_p} \quad (2)$$

Substituting eqn. (1) into eqn. (2) yields:

$$D_n(1-P)(T_a - G/D_i) + G = D_n(1-P_p)(T_p - G/D_i) + G \quad (3)$$

which results in the expression for the pressed part porosity:

$$P_p = 1 - (1-P)\frac{T_a - G/D_i}{T_p - G/D_i} \quad (4)$$

The weight of the pressed area is:

$$W_p = \frac{W_a S_p}{S_a} \quad (5)$$

The weight of the unperforated strip (*i.e.*, that which is wiped clean of sinter) is:

$$W_s = (S - S_a - S_p)D_i T_s \tag{6}$$

and the total weight of the plaque ($W_a + W_p + W_s$) is:

$$W = p(S_a + S_p)\left[D_n(1-P)\left(T_a - \frac{G}{D_i}\right) + G\right] + (S - S_a - S_p)D_i T_s \tag{7}$$

This relationship permits process control by weight and thickness measurements so that the porosity is in the desired range. In the design of sintered plate cells, the cell capacity can be predicted from the product of void volume and loading level [6]. The total void volume in cell electrodes is as follows:

In the active area: $V_a = nS_a P(T_a - G/D_i)$ (8)

In the pressed area: $V_p = nS_p P_p(T_p - G/D_i)$ (9)

Combining eqn. (4) with eqn. (9):

$$V_p = nS_p[P(T_a - G/D_i) - (T_a - T_p)] \tag{10}$$

The total void volume in the cell electrodes (V_o) is therefore:

$$V_o = V_a + V_p = n(S_a + S_p)P(T_a - G/D_i) - nS_p(T_a - T_p) \tag{11}$$

In the impregnation of sintered plaques the active material is forced into the void volume in the sinter. The active material fills about 60% of this volume, the balance is left for the electrolyte. Shortage of electrolyte will result in loss of capacity and an increase in cell resistance, with a consequent reduction in cell discharge voltage and cycle life [7]. It is therefore recommended that different cell sizes maintain a fixed ratio between the active material volume and the electrolyte volume. Thus, for a fixed active material fill ratio, the cell capacity will be proportional to the void volume in the raw sinter and to the sinter thickness (see eqn. (8)). Again, because of the need to maintain room for sufficient electrolyte in the cell, it is necessary to limit the active material loading level. It has also been stated [8] that the positive active material utilization increases up to 0.309 A h cm^{-3} of plate. In addition, it should be noted that, although the utilization of active material is greater in thinner plates [8, 9], the cell capacity increases with plate thickness. Under these conditions the capacity becomes:

$$C = KV_a = KnS_a P(T_a - G/D_i) \tag{12}$$

Experimental validation

As part of routine quality control policy, raw, sintered plaques taken from production over a period of six months were checked. The goal was to assure an 83% porosity. At the same time the weight per unit area and the

thicknesses of active parts were also monitored. With an average specific weight of substrate (G) of 0.0305 g cm^{-2} and other known quantities substituted in eqn. (1), the weight per unit active area is obtained:

$$\frac{W_a}{pS_a} = 8.9(1 - 0.83)(T_a - 0.0305/7.95) + 0.0305 = 1.513T_a - 0.0247$$

Figure 2 plots this relationship using measured information and verifies the above calculated result with a correlation coefficient of 0.997. Thus, eqn. (1) may be used as a simple, inexpensive way to determine average porosity.

In the same quality checks the positive plate capacities, areas, and thicknesses, were tabulated for various sizes of production cells. The average of the capacity per unit void volume (K) was found to be 0.39 A h cm^{-3}. Applying the various factors already tabled above to eqn. (12) the capacity per unit active area as a function of the active part's thickness is given by:

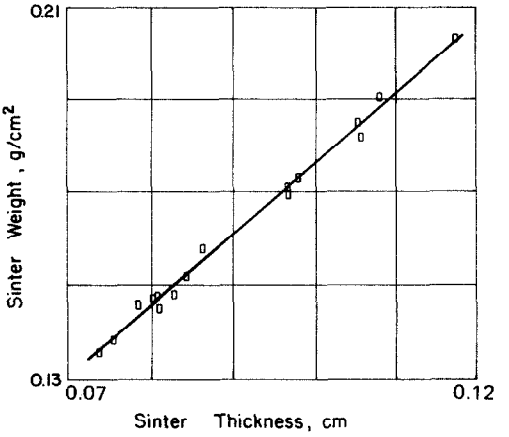

Fig. 2. Sintered plaque weight per unit active area *vs.* sinter thickness.

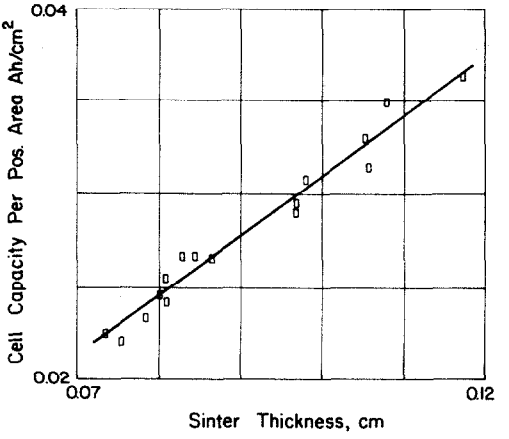

Fig. 3. Average capacity of cells per positive electrode area *vs.* sinter thickness.

$$\frac{C}{nS_a} = 0.39(0.83)(T_a - 0.0305/7.95) = 0.324T_a - 0.001\,24$$

Figure 3 plots this relationship using measured information and verifies the calculated results for various electrode thicknesses with a correlation coefficient of 0.983.

Conclusions

The design of nickel–cadmium sintered plate cells is facilitated by simple void volume considerations. These considerations result in equations which predict sintered plaque weights and capacities of cells of different sizes. With adjustment of the coefficients for starved or flooded systems and for different cell formation procedures, the equations are useful tools in the design of both sealed and vented cells.

List of symbols

C Cell capacity (A h)
D_i Density of substrate material = 7.95 g cm^{-3} for steel (g cm^{-3})
D_n Density of nickel = 8.9 g cm^{-3} (g cm^{-3})
G Weight of perforated substrate per unit area (g cm^{-2})
K Capacity per unit sinter void volume (A h cm^{-3})
n Number of electrodes per cell
p Number of electrodes per plaque
P Sinter porosity = Void volume divided by apparent sinter volume
P_p Sinter porosity in pressed area
S Total plaque area (cm^2)
S_a Active area of electrode (cm^2)
S_p Pressed area of electrode (cm^2)
T_a Thickness of electrode in the active area (cm)
T_s Thickness of unperforated strip (cm)
V_a Void volume in active area of sintered electrodes (cm^3)
V_o Total void volume of sintered electrodes (cm^3)
V_p Void volume in pressed area of sintered electrodes (cm^3)
W Total weight of plaque (g)
W_a Weight of active area (g)
W_p Weight of pressed area (g)
W_s Weight of unperforated strip (g)

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