THEORETICAL STUDY OF A COMPOSITE ELECTRODE USING AN INTERCALATION COMPOUND: INFLUENCE OF THE PARTICLE SIZE DISTRIBUTION ON THE DEPTH OF DISCHARGE

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Summary

The influence of the particle size distribution in a composite electrode has been theoretically studied for constant current discharge.

For Fermi, Gauss, and Gamma distributions, a good estimate of the depth of the first discharge can be obtained using an average grain size corresponding to the maximum of the volume distribution. A study of the influence of the sifting cut-off point is also discussed.

1. Introduction

With the revived interest in high energy density batteries, solid state devices using lithium as a negative electrode, and intercalation compounds, have been actively studied.

Most of the research [1 - 3] was initially focused on electrochemical mechanisms or on the prediction of the performances of each cell constituent. More recently, Atlung [4] has theoretically considered the technological aspects and their influence on the depth of the first discharge for secondary batteries. He confirmed that the best efficiencies for a composite electrode were obtained from 3D compounds [4, 5], a fact experimentally verified by Uteani [6] on manganese dioxide batteries.

In this paper, a theoretical study of the influence of the particle size distribution of an intercalation material in a composite at constant current is presented, using the same assumptions as Atlung [5], and neglecting the transference number of the anion that could lead to salt depletion in the composite.

2. Mathematical model and treatment in the case of galvanostatic method control

We have studied a composite electrode consisting of a mixture of an electrolyte, a "host" material, and an electronic conductor. The surface of

each particle was considered as equipotential so that the interfacial inter-calation ratio, y, is the same for each particle.

From this hypothesis and taking the sum of partial intensities, the Laplace transform can be calculated in the following manner:

$$\bar{y} = \frac{\sum\limits_{i=0}^{j} Ia_i}{nFDC^0 \sum\limits_{i=0}^{j} S_i \dfrac{I_{3/2}[a_i(p/D)^{1/2}]}{I_{1/2}[a_i(p/D)^{1/2}]}} \quad \text{for } x_i = a_i \tag{1}$$

The discharge depth was calculated from the highest intercalation ratio. At the surface of each grain we obtain: $y_i = y = 1$ for $t = t_d \; \forall \; i$.

The inverse transform of this function is unknown and we therefore approximated it by a sum of exponentials with known inverse transforms.

This numerical method requires the calculation interval for the function given in eqn. (1) to be determined. The limits of this interval have been set by calculating the discharge depth for a monodisperse electrode at different discharge currents. We compared the results with those obtained by Atlung [4] under the same conditions. This method seems to be limited in accuracy only by the computer (MICROMACHINE 2006 SYMAG). We solved the different equations for discharge rates between $C/5$ and $C/200$.

The first discharge depth was calculated for the following particle size distributions: GAUSS, FERMI and GAMMA. The results are shown in Figs. 1 - 3.

3. Discussion of results

In all cases, a good estimate of the first discharge depth can be made using an average grain size corresponding to the maximum of the volume distribution (Fig. 1).

The reason for this is quite clear if we think in terms of available sites for intercalation species.

For the distribution with various standard deviations (Fig. 2), this dis-charge depth does not vary markedly from one curve to another; the dis-charge depth always corresponds to the maximum of the volume distri-bution.

We also studied the influence of some large particles in a monodisperse distribution (Table 1). We observed a significant decrease in the discharge depth with the addition of a small number (1 or 2%) of large particles.

We also tried to simulate a sifting obtained by removing the upper part of the Gaussian distribution (Fig. 3). A noticeable effect is observed only when the largest particles are eliminated. The variations of the volume maxi-mum are nearly zero under these conditions and, at the same time, the varia-tions of the depth of discharge are important.
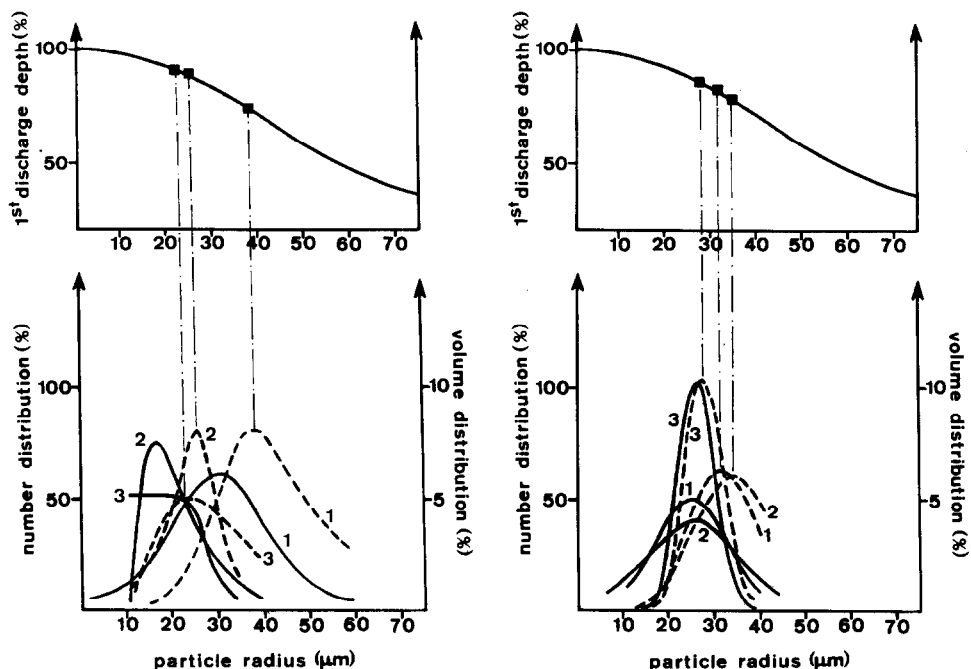
Fig. 1. Influence of the type of number distribution on the first discharge depth (τ = 10 h, $D = 10^{-10}$ cm^2 s^{-1}) 1, GAUSS; 2, GAMMA; 3, FERMI. Upper: 1st discharge depth *vs.* grain radius. ——, mono granulometric distribution; ■, distribution 1, 2 or 3. Lower: number (——) or volume (— — —) distribution *vs.* grain radius.

Fig. 2. Influence of the standard deviation of the Gaussian distribution on the first discharge depth (τ = 10 h, $D = 10^{-10}$ cm^2 s^{-1}). Upper: 1st discharge depth *vs.* grain radius. ——, mono granulometric distribution; ■, distribution 1, 2 or 3. Lower: number (——) or volume (— — —) distribution *vs.* grain radius.

TABLE 1

Influence of a few large particles in a monodisperse distribution
$D = 10^{-10}$ cm^2 s^{-1}; τ = 10 h.

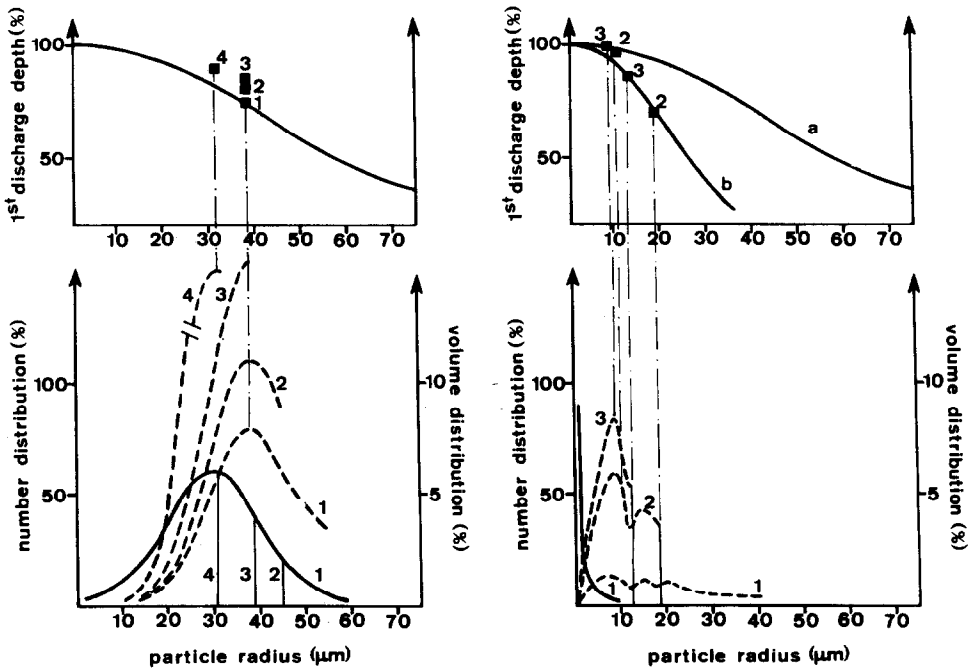| Small grains		Large grains		Discharge depth
Radius	Number	Radius	Number	
20	100	0	0	95.3
20	99	30	1	95
20	98	30	2	94.7
20	99	60	1	84.6
20	98	60	2	77.7

Fig. 3. Influence of sifting on the first discharge depth ($\tau = 10$ h, $D = 10^{-10}$ cm^2 s^{-1}). Upper: 1st discharge depth *vs.* grain radius. ———, mono granulometric distribution; ■, distribution 1, 2, 3 or 4. Lower: number (———) or volume (— — —) distribution *vs.* grain radius.

Fig. 4. Influence of the current intensity and of sifting on the first discharge depth for MoO$_2$ powder (VENTRON). Upper: 1st discharge depth *vs.* grain radius. (a) $\tau = 10$ h; (b) $\tau = 2$ h. Lower: distribution *vs.* grain radius. 1, Number (———) or volume (— — —); 2 and 3, volume distributions after sifting.

Figure 4 represents the size distribution compared with the discharge depth for commercial MoO$_2$ powder (VENTRON). Low current intensities induce a discharge depth near to those at the volume maximum. In this case, the intercalation ratio for all the grains is approximately 1 at the end of discharge.

With high current intensities, the discharge depth is less and its value corresponds approximately to the volume value obtained for the largest grain size (cut-off point).

List of symbols

a	Particle radius
C^0	Concentration maximum of empty sites
D	Diffusion coefficient
F	Faraday constant
I	Current intensity
$I_{3/2}\,I_{1/2}$	Modified Bessel function of the first kind and of the order 3/2 or 1/2
n	Number of electrons exchanged in the electrochemical process
p	Laplace parameter
S_i	Particle area
t	Time
t_d	Discharge time
$\bar{y}$	Laplace transform of the intercalation ratio y
τ	Stoichiometric discharge time

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