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EXAMINATION OF THE GRAPHITE ADDITIVES TO ELECTRODES

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Summary

The electrodes of most power sources are made by some powder technology technique. To improve the characteristics of accumulators, we must find relationships between the characteristics of the powdered electrode materials and the electrochemical parameters of the accumulator. We have examined the connection between the features of powdered graphite and its applicability to power sources. A plastic bonded, Ni/Cd accumulator, positive electrode was chosen as a model. We chose oxidation by heat treatment as a means of characterizing the electrochemical behaviour of the graphites. The features of powdered graphite, and the connection between the powder characteristics and the electrochemical behaviour of the final cell, may be characterized mathematically.

Physical tests and electrochemical measurements show that a graphite possessing an average oxidizability is the best material to use. If the graphite oxidizes easily it is reduced readily electrochemically. A graphite which is hard to oxidize, however, is usually very coarse and utilisation of the active material reduces exponentially with its addition.

Introduction

The electrodes of most power sources are made by some powder technology technique. To improve the characteristics of accumulators made with these electrodes, and also to obtain greater knowledge of the functioning of accumulators, it is not enough to examine the electrodes by electrochemical methods. We must also determine the connection between the characteristics of the powdered materials and the electrochemical parameters of the accumulators [1, 2]. As particle size distributions are usually changed in the direction of increasing dispersion, and electrodes are a porous system with a high specific surface, a knowledge of the powder features may enable electrodes to be improved.

Active materials of high dispersion are used to increase the efficiency of electrodes. They are placed on a metal grid, rod and net, or in a metal pocket.

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Generally, both the discharged positive and the discharged negative active materials are bad conductors. Therefore, a powder with good electrical conductivity is often mixed with the active materials of power sources. Such conducting materials may, for example, be a metal powder or one of the different modifications of carbon, *e.g.*, carbon black and graphite.

By comparison with other carbon powders graphite has the highest conductivity and chemical resistance. Its density is less than that of most metals and its chemical resistance higher. Graphite powder is used in primary mercury(II) oxide/Zn and Ag(I) oxide/Zn button batteries, for example, where it is mixed with the metal oxides. Other than in the case of sintered frame electrodes, conducting powders, mostly graphites, are mixed with the active materials in all types of Ni/Cd accumulators.

In our experiments a plastic bonded positive electrode of the Ni/Cd accumulator was chosen as a model [3, 4], but the methods used and the conclusions drawn may also be applied to other power sources.

Experimental

Examination of graphites

Graphites may be oxidized by strong oxidizers but oxidation does not always lead to a reduction in weight; in the case of infiltration by donor radicals it may even increase the weight.

We have tried to oxidize different types of graphite chemically and to correlate the treatment with their electrochemical behaviour. The results were ambiguous, so resulting from our observations and published information [5, 6], we turned our attention to oxidation by heat treatment. We first measured the reduction in weight of the original 2.00 g of powdered graphite. The tests were carried out in air, over a range of temperatures, on the same graphite sample. The samples were held at each temperature for thirty minutes then cooled in a desiccator. Graphites of different origin have different degrees of dispersion and different levels of impurity. To promote comparison we reduced the graphite samples to fractions of below 45 μm, between 45 and 63 μm and 63 - 100 μm. We also measured the powder characteristics of the graphites.

Examination of the powder characteristics

To measure the bulk density we poured a known weight of the powder into a measuring cylinder which was then tapped until the volume remained constant. The specific resistance (ρ), measured in a cylindrical sample holder, with a 10 kg cm^{-2} load and a current (A) of 100 mA, is given by:

$$\rho = \frac{Vq}{Al} \tag{1}$$

where V is the voltage drop, q the cross section and l the length.

For measuring the specific surface (S) of the powder, air was blown through a powder roll compacted to a definite volume and the time of flow

(t) was measured, and is given by:

$$S = K_1 d \left[t \left(1 - \frac{m}{K_2 d} \right)^3 \right]^{1/2} \tag{2}$$

where K_1 and K_2 are constants, d is the density of the powder, and m is the mass.

Our results were also checked by the BET method. We not only measured the specific surface of the original graphites but also changes as a function of the heat treatment temperature. The temperature was raised at 80 °C/min and reduced at 30 °C/min. The sample was held for 30 min at the prescribed temperature (+3 °C and 0 °C). After cooling, the sample was placed in a desiccator, and the specific surface was measured next day.

Examination of the active material and electrodes

A fixed quantity of different graphites was always added to the active material. The samples were blended as usual, then the bulk density of the active material was measured. Disks (15.48 cm^2; 0.2 cm thick) of the active material were pressed at 0.65 t cm^{-2}. The density of the disk was measured by a picnometer and the specific resistance was measured, at different weight loadings, between two 1 cm^2 copper disks at a current of 500 mA. The specific resistance was calculated from eqn. (1). The capacity of the active material disk (in A h) was also measured, in a high alkali excess, between plastic bonded Cd auxiliary electrodes for up to ten cycles. Plastic bonded electrodes were made from powder mixtures of the active material containing different graphites with a capacity of about 2 A h. The specific resistance of the electrodes was measured using the same method as that described for the disks. Test cells were constructed from prepared electrodes, wherein the capacities of two Ni electrodes were measured with three Cd electrodes [7].

Results and discussion

The graphites of different origin were oxidized by heat treatment. Figure 1 presents the relative rate of weight reduction of three powder graphites and a flake graphite. All are plotted with reference to graphite I at 450 °C. The graphites of different origin have different oxidizability as Fig. 1 suggests. With a powder graphite I specific surface of 0.98 m^2 cm^{-3}, of powder graphite II of 1.49 m^2 cm^{-3} and of powder graphite III of 1.56 m^2 cm^{-3}, we can see from the results that reducing the dispersion reduces the oxidizability of graphites. Figure 2 shows the characteristics of fractions under 45 μm as a function of the specific surface.

The apparent density (d_a) decreases as a function of the specific surface (S), given by:

$$d_a = b_3 \exp(-a_3 S) \tag{3}$$

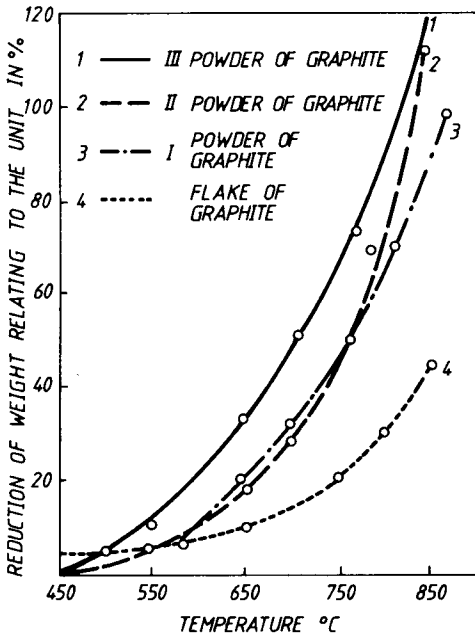where a_3 and b_3 are constants.

Fig. 1. Reduction in weight of graphites of different origin as a function of the heat treatment temperature.
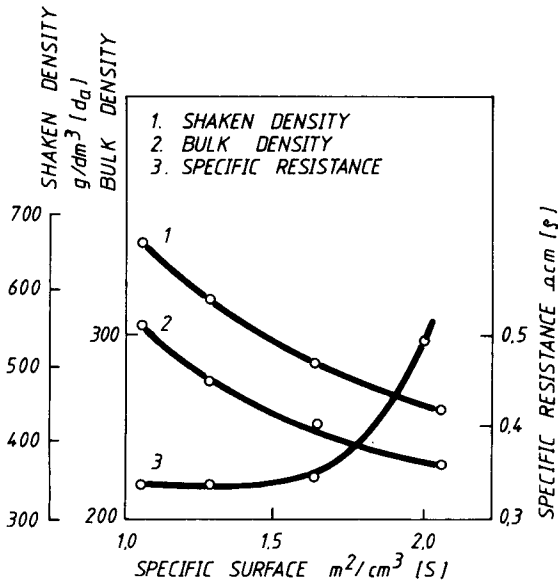

Fig. 2. Powder characteristics as a function of the specific surface.

In the case of the bulk density, $a_3 = 0.30$
$$b_3 = 411$$

In the case of the "tapped" density $a_3 = 0.56$
$$b_3 = 1220$$

The specific resistance (ρ) in the case of the specific surface $S \leqslant 1.7$ is:

$$\rho = a_4 S + b_4 \tag{4}$$

where a_4 and b_4 are constants: $a_4 = 1.69 \times 10^{-3}$
$$b_4 = 0.33$$

In the case where $S \geqslant 1.7$ the specific resistance is given by:

$$\rho = b_5 \exp(a_5 S) \tag{5}$$

where $a_5 = 1.2$
$$b_5 = 0.05$$

From the Figure and the equations we can see that the specific resistances of the graphites we tested were practically constant over a wide range of specific surfaces. They then increase exponentially. The specific resistance of graphites depends not only on the function of the surface, i.e., on the function of dispersion and the shape of the grains, but also on the purity of the graphite.

Figure 3 shows the specific resistance (ρ) of graphite as a function of the amount of impurity (I).
For $I \leqslant 4\%$ the relationship is linear:

$$\rho = a_6 I + b_6 \tag{6}$$

where $a_6 = 0.06$
$$b_6 = 0.17$$

but when $I > 4\%$ it becomes exponential:
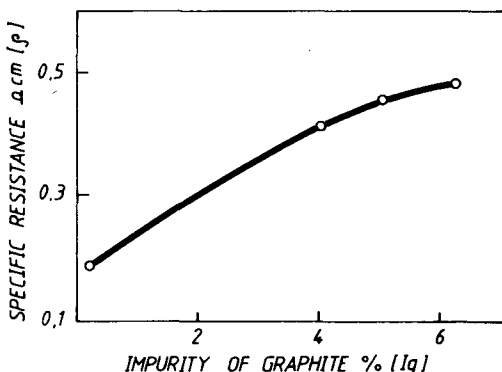
$$\rho = b_7 \exp(a_7 I) \tag{7}$$

Fig. 3. The specific resistance of graphites as a function of their impurity.

where $a_7 = 0.07$
$b_7 = 0.31$

Increasing the amount of impurity in the graphite, therefore, decreases its conductivity. The influence of grain size on the oxidizability was tested on graphite I, which proved to have the highest resistance after the first heat treatment.

Figure 4 presents the reduction in weight (W_d) of the three fractions of graphite I as a function of the heat treatment temperature. We can see that for graphites of identical chemical composition the oxidizability increases with the degree of dispersion, and the weight is given by:

$$W_d = a_8 t^2 - b_8 \qquad (8)$$

This is valid over the complete range of temperature for the two finer graphite fractions and the graphite 63 - 100 μm when $t > 650\ ^\circ$C.
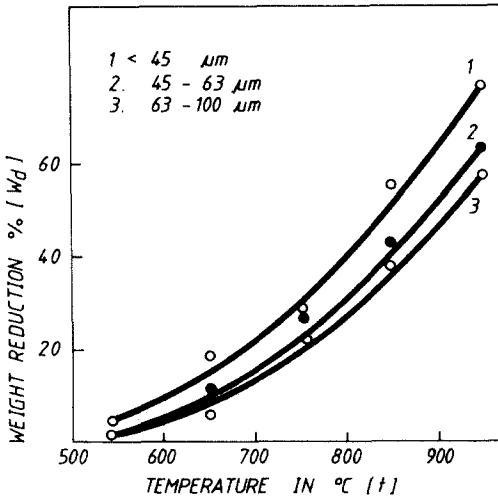

Fig. 4. The reduction in weight of the fractions of graphite I as a function of the heat treatment temperature.

The constants are:

fraction under   45 μm $a_8 = 1.19 \times 10^{-4}$
$b_8 = 31.3$

45 - 63 μm $a_8 = 1.01 \times 10^{-4}$
$b_8 = 26.9$

63 - 100 μm $a_8 = 9.88 \times 10^{-5}$
$b_8 = 33.1$

To monitor the oxidizability of graphite further we measured the change in specific surface area as a function of the heat treatment temperature. This is
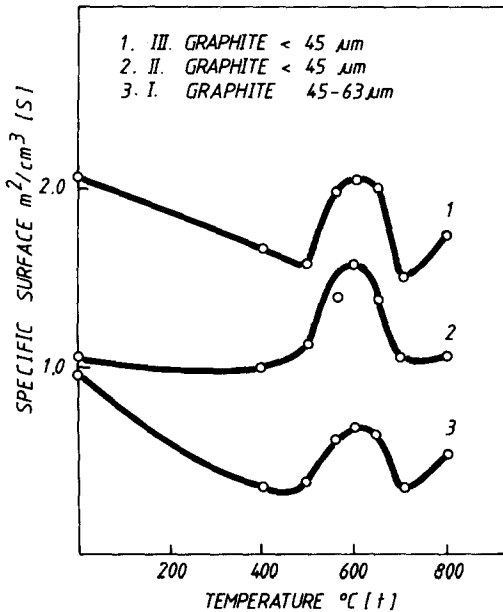
Fig. 5. The changing of the specific surface as a function of heat treatment temperature.

shown in Fig. 5. Model materials were: 45 μm of graphites I and III and 45 - 63 μm of graphite I. We can see that the specific surface decreases at low temperatures (400 - 500 °C) compared with the original graphites. With increasing heat treatment temperature the specific surface passes through a maximum at about 600 °C whatever the origin of the graphite.

The range between 500 and 700 °C is the most interesting. For 500 $\leqslant$ $t \leqslant$ 700 °C the specific surface area is given by:

$$S = S_0 + a_9(t - t_0)^2 \tag{9}$$

$t_0 = 600$ °C and S_0 is the height of the parabola.

For graphite III under 45 μm $a_9 = -5.0 \times 10^{-5}$

For graphite II under 45 μm $a_9 = -4.8 \times 10^{-5}$

For graphite I 45 - 63 μm $a_9 = -3.3 \times 10^{-5}$

The absolute value of a_9 decreases with increasing grain size.

We measured the specific surface of the original graphites following normal storage, and the heated graphites on the day after the heat treatment or, at least, after allowing them to cool. We also measured the specific surface of the original graphites after drying them for 24 h at 105 °C and allowing them to cool. The values of the coarsest graphite specific surface were the same within the error limit of the test. In the cases of the two finer graphite samples the maximum values of the specific surfaces were 50 - 70% higher and the maximum moved to 650 °C, while for the coarse graphite it
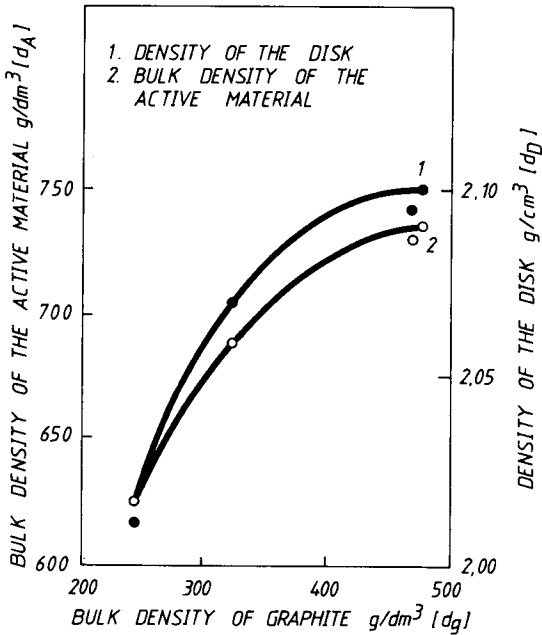
Fig. 6. The bulk density of active material and the density of the disk as a function of the bulk density of graphite.

remained at 600 °C. The difference in the results between the two testing methods may be associated with the adsorption of graphites. We then examined the characteristics of the active material modified by the different graphites.

Figure 6 gives the relationship between the bulk density of the graphite (d_g) and the bulk density of the active material (d_A), and also presents the density of the disk (d_D).

$$d_A = b_{10} \exp(a_{10} d_g) \tag{10}$$

$$d_D = b_{11} \exp(a_{11} d_g) \tag{11}$$

Both parameters of the active material change exponentially with the bulk density of the graphite. For the bulk density of the active material:

$$a_{10} = 6.64 \times 10^{-4}$$

$$b_{10} = 538$$

For the density of the active material disk:

$$a_{11} = 1.63 \times 10^{-4}$$

$$b_{11} = 1.94$$

Figure 7 presents the changes of capacity (C) and the specific resistance with the bulk density of the active material. The disks were made by using graphite I and show that in

$$C = b_{12} \exp(a_{12} d_g) \qquad (12)$$

$$a_{12} = 1.01 \times 10^{-3}$$

$$b_{12} = 312.4$$

The bulk density of the active material increases with the coarser graphite. Thus, the capacity of the active material decreases exponentially with the coarseness of the graphite. As identical quantities of graphite were added in all cases less active material grains are in contact with the conducting graphite grains as the coarseness increases and the utilisation of the active material is decreased. The change of the specific capacity of the active material (C), was determined as a function of the graphite impurity. The results are plotted in Fig. 8.

The relationship between the capacity of the active material and the graphite impurity (I_g) was shown to be:

$$C = \frac{a_{13}}{I_g} + b_{13} \qquad (13)$$

In the system that we investigated the value of the constants were:

$$a_{13} = 4.40$$

$$b_{13} = 139.4$$

In Fig. 9 the specific resistance of two electrodes containing two graphite fractions under 45 μm, and with different bulk density, are shown as a
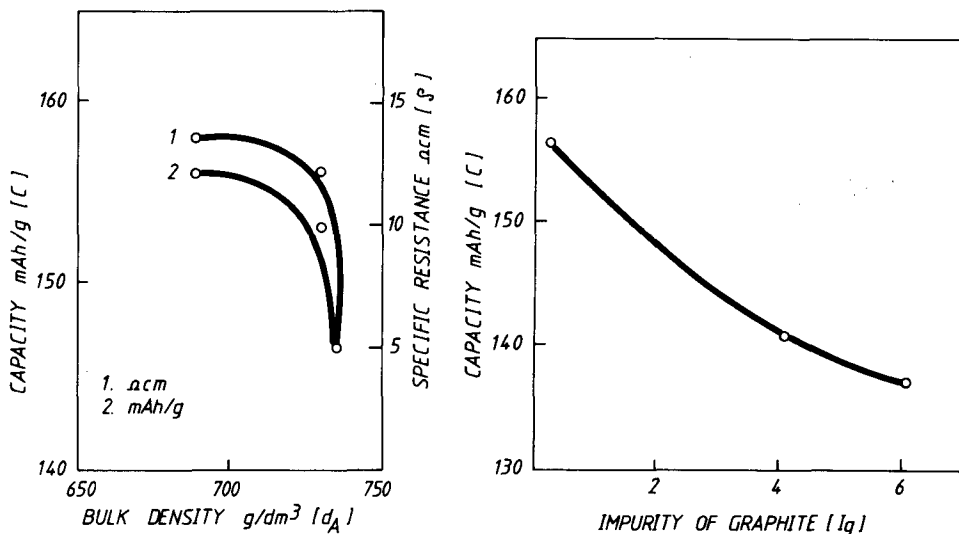

Fig. 7. The capacity and the specific resistance of disks as a function of the bulk density of the active material.

Fig. 8. The specific capacity of the active material as a function of the impurity of the graphite.

function of weight load (curves 1) and graphite impurity (curves I). The Figure presents the parameters of electrodes which have not been wetted in alkali and are not formed. We can see from the Figure that electrodes having the graphite with the higher dispersion have the higher specific resistance, and in both cases the specific resistance increases with the impurity in the graphite.

Figure 10 shows the capacity of the test accumulators as a function of the graphite impurity. Equation (13) is also valid in this case with the same constant values, and therefore can be applied to clean active material disks and plastic bonded electrodes.

Table 1 presents the capacity of experimental accumulators made from graphites I and II powder of less than 45 μm and the characteristics of graphite powder. We have shown (Fig. 7) that the capacity of the active material decreases exponentially with increasing graphite grain size and is inversely proportional (Figs. 8, 10) to the graphite impurity. We can also see from
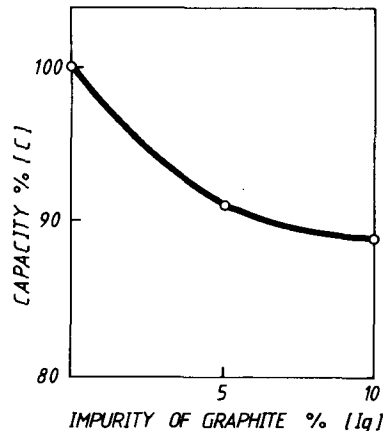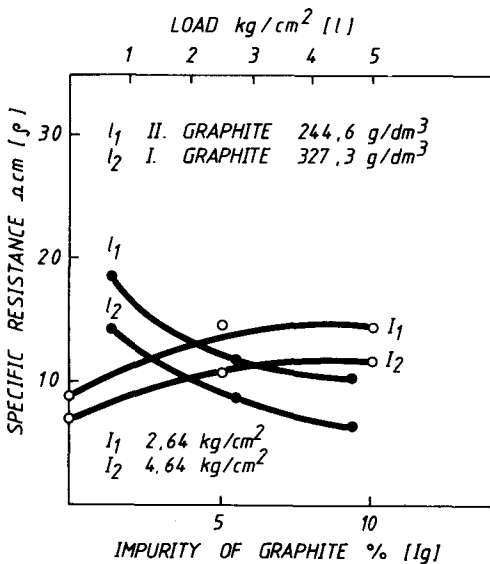

Fig. 9. The specific resistance of the electrodes as a function of load (l) — ● —, and as a function of graphite impurity (I_g) — ○ —.

Fig. 10. The capacity of the testing accumulators as a function of graphite impurity.

TABLE 1

Type of graphite	I under 45 μm	II under 45 μm
Bulk density (g dm^{-3})	327.3	244.6
Impurity (%)	0.26	4.1
Capacity (A h)	4.55	4.27
C_5 (%)	100	93.85

Table 1 that impurities in graphite have a greater influence on the capacity of the electrode than does the dispersion.

Conclusions

The optimum conductor material in accumulator electrodes must have low specific resistance, a high specific surface, and be resistant to oxidation. These requirements, however, are conflicting ones and must be evaluated simultaneously. We chose oxidation by heat treatment to characterize this effect of the electrochemical behaviour of electrodes containing graphite. This was associated with measurements of the specific surface of the tempered active material. We also investigated the effect of graphite impurity. According to the physical tests and electrochemical measurements, a graphite possessing an average oxidizability is the best material to use. If it oxidizes easily it is also reduced too strongly electrochemically. A graphite which is difficult to oxidize, however, is often very coarse and the utilisation of the active material reduces exponentially with its incorporation. There is, in addition, an inverse connection between the impurity in the graphite and the capacity of the electrodes. The specific surface of a graphite initially increases but subsequently decreases as the heat treatment temperature increases. The maximum is a characteristic of the particular graphite.

List of symbols

ρ	Specific resistance (Ω cm)
V	Voltage difference between the two edges of the column (V)
q	Cross-section of the powder column (cm^2)
l	Height of column (cm)
A	Currents (A)
S	Specific surface (m^2 cm^{-3})
K_1 and K_2	Apparatus constants
d	Density of the powder (g cm^{-3})
t	Flowing time in seconds (s)
m	Weight of the powder (g)
d_a	Apparent density (g dm^{-3})
W_d	Reduction of weight relating to the unit (%)
d_A	Bulk density of active material (g dm^{-3})
d_D	Density of the disk (g cm^{-3})
d_g	Bulk density of graphite (g dm^{-3})
C	Specific capacity of the active material (mA h g^{-1})
I_g	Impurity of graphite (%)

References

1 Á. Veres and G. Csath, *2nd Symp. on Particle Size Analysis and Powder Technology, Hungary, 1983*, Vol. I, pp. 161 - 167.

2 Á. Veres, J. Ágh, L. Csorba and M. Benedek, *PORANAL' 80, Symp., Hungary, 1980,* pp. 24 - 26.
3 S. Kulcsár, J. Ágh, Á. Veres and Z. Bujdosó, *J. Power Sources, 8* (1982) 55 - 59.
4 J. Mrha, M. Musilova, J. Jindra, M. Polydorova and J. Peizker, *J. Power Sources, 8* (1982) 3 - 8.
5 U. Wiesman, *Steinkohle und Koks,* Berlin, 1965.
6 R. H. Knibbs and J. B. Morris, *Third Conf. on Industrial Carbons and Graphites, London, 1970,* pp. 297 - 308.
7 S. Kulcsár, P. Horváth, G. Csath and M. Smaroglay, *J. Power Sources, 8* (1982) 61 - 65.