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Analysis of porous alkaline Cd-electrodes. IV. Optimization of current efficiency

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Optimization of the electrode-thickness, porosity and the amount of active material necessary for a defined electrode polarization is carried out with a mathematical model on porous Cd-electrodes. Three different problems were formulated for a constant current-load, and a specified final total polarization in order to maximize the utilization of active materials. The results obtained show that the best high rate electrodes (100 mA cm^{-2}) are high porosity electrodes with the half-width thickness in the interval of 0·10–0·18 cm depending on the formulated optimization problems.

Nomenclature

d	half electrolyte-channel width, cm
i	current density, A cm^{-2}
I	current load, A
K	constant defined by Equation 7, A min
l	half electrode-thickness, cm
N	electrode space division number
q	volume capacity with porosity included, A min cm^{-3}
q_0	theoretical volume capacity, A min cm^{-3}
Q(a)	capacity within the system volume, projected on the electrode surface perpendicular to the channel current, A min cm^{-2}
Q(b)	capacity within the system volume, projected on the electrode base area, A min cm^{-2}
ϵ	porosity
η	efficiency
*	optimal

1. Introduction

The materials used in battery electrodes are usually expensive, and this motivates the search for more efficient electrode designs. Electrodes in high rate applications have generally the poorest utilization of the active material and it is therefore important to analyze their design. Attention is drawn here to the porous high rate Cd-electrodes which have been presented recently [1] as an example of a simple optimization analysis.

The distribution of the active material in the geometrical cell body is important in the design of efficient batteries. The problem of distribution can conveniently be divided into two groups of problems: local and global, depending on their influence on the physical cell design. A local design problem can be given by an attempt to find the combination of porosity and electrode thickness which gives the best utilization of the active material. An example of a global electrode design problem is the treatment of the compromise between a small number of large electrodes and a large number of small electrodes for various amounts of active material.

The porous electrode which is to be optimized in this analysis has an open and planar structure. The open structure gives an electrode free from the diffusion and current restrictive geometrical influences which often are associated with commercial electrode constructions in which the active materials are enclosed in various ways. The envelopes are usually of the perforated pocket type [2].

By selection of the undisturbed electrode structure it is possible to obtain results which represent the ultimate limits of criteria for a chosen sample of the active material. The open structure thereby

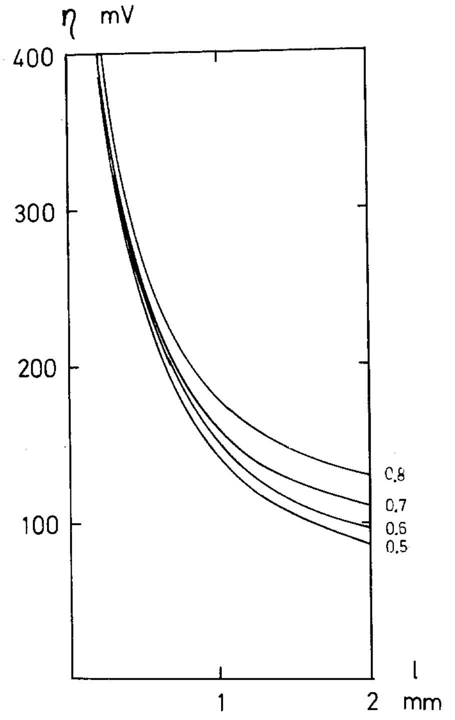

Fig. 1. Calculated initial time overpotentials shown as functions of the electrode-thickness l for a current load of 100 mA cm^{-2}. The parameters are the values of porosity for charged electrodes.

represents the ideal structure which can be of value when compared with the technical electrodes.

2. Analysis

From the theoretical and experimental analysis of porous electrodes it is well-known that high current loads give non-uniform and poor utilization of the active materials [3, 4]. Non-uniform current distributions occur predominantly for thick electrodes. Therefore an obvious way to increase the utilization of the active material would be to decrease the electrode-thickness. A decrease in the electrode thickness in general leads to an increased electrode polarization at constant load conditions. Fig. 1 shows the importance of the electrode thickness for the polarization at a constant current load. Fig. 1 also shows that it is possible to obtain a low polarization with a large amount of the active material. It is possible to formulate several problems with almost the same goals, and it is necessary to some extent to discuss the problem-analysis and the influence of the various criteria on the electrode design.

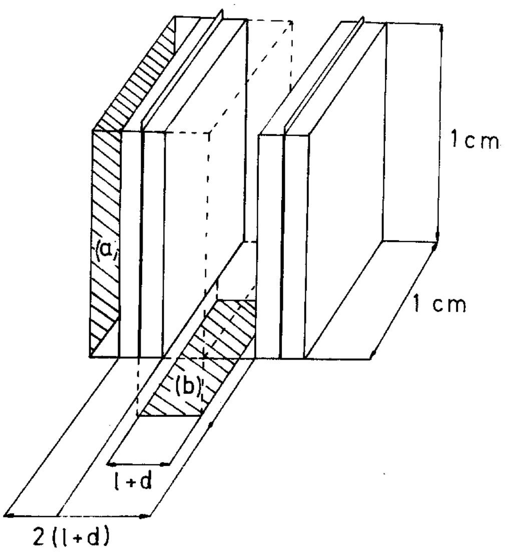

Fig. 2. The base-electrode with the assumed system-volume. Surface (a) is the electrode cross-section area perpendicular to the electrode-current direction. Surface (b) is the bottom-projection of one symmetrical part of the electrode with one half of the electrolyte-channel included.

For electrodes based on expensive materials it is obvious that current-efficiencies should be compared. It is convenient to make the comparison of efficiency for various constant current loads and for various final polarization levels. The polarization levels are to be chosen with regard to specified technical applications. A polarization of 200 mV is in this work assumed to be reasonable for high rate discharges (100 mA cm^{-2}). The ratio of the capacity consumed for a given maximum polarization to the total available capacity gives the utilization efficiency (Equation 5). Another way is to compare efficiencies at a fixed interval of time. The latter is usually applied in cranking applications.

The given concept of current efficiency gives no information on the way in which an electrode is to be constructed, and in order to overcome this lack of information it is necessary to describe the utilization of the electrode volume. For a local optimization problem, which is the main interest here, it is practical to let the system volume be composed of a half-electrode, l, together with a half-electrolyte channel, d, including the current collector in the electrode. Fig. 2 shows the system volume for one electrode. From this division of the system volume there is only the electrode thickness in combination with the electrode porosity as variables to affect the capacity. The capacity within the system volume is Q A min. The amount of active material corresponding to Q can be related to two different projections which both express compactibility. When the capacity Q is projected perpendicular to the load-current direction, the measure Q(a) A min cm^{-2} is defined. The measure Q(b) A min cm^{-2} is defined from the projection of capacity Q on the base area. In Q(b), consideration is given to the effect of passive construction elements such as the channel electrolyte and the collector, which is not the case within Q(a). Q(b) belongs more than Q(a) to the global analysis where the electrode height together with the electrode thickness is the central problem. Therefore attention is drawn here primarily to the measure Q(a) as it is a local problem.

2.2. *Relations between design variables and capacity*

The equation which gives the capacity of the system volume is:

$$Q(\mathrm{a}) = q \cdot l, \tag{1}$$

where q is the volume capacity of the active material in A min cm^{-3}. The system volume considered here, is $l \cdot 1^2\,\mathrm{cm}^3$ (1 cm^2 electrode area).

The capacity q is dependent on the porosity and the theoretical capacity q_0 according to Equation 2:

$$q = q_0(1-\epsilon). \tag{2}$$

With q from Equation 2 introduced in Equation 1, Q(a) is explicitly expressed in l and ϵ, which is shown in Equation 3:

$$Q(\mathrm{a}) = q_0(1-\epsilon)l. \tag{3}$$

Q(b) is obtained in an analogous way:

$$Q(\mathrm{b}) = q_0(1-\epsilon)\frac{l}{l+d}. \tag{4}$$

A comparison between Equations 3 and 4 for a constant electrolyte-channel and collector shows that Q(a) and Q(b) are linearly proportional.

2.3. *Variable constraints*

In all optimization analysis it is necessary to specify the allowed intervals of the design variables. To be considered in the following are the limits for the electrolyte channel d, the charged electrode porosity ϵ, the theoretical capacity q_0 and electrode thickness l.

The width of the electrolyte channel d has the lower limit determined by the buffer capacity of the electrolyte against concentration changes. This argument can be neglected at short-time discharges. A common channel measure with the collector included is about 1 mm, which corresponds to $d = 0{\cdot}5$ mm according to the definition used for d. The interval $0{\cdot}25 \leqslant d \leqslant 0{\cdot}5$ is selected here.

The electrode porosity ϵ has an upper limit dependent on mechanical properties. The upper porosity limit is 0·85 which corresponds to the upper limit in the experimental investigations made on this active material [1]. The lower porosity limit is 0·40 and is selected with respect to the drastic reduction of the accessible active surface which occurs below this value. The interval $0{\cdot}4 \leqslant \epsilon \leqslant 0{\cdot}85$ corresponds to the design porosities allowed here for charged electrodes.

The theoretical capacity q_0 is given with regard to the amount of active material in the solid state phase. In this investigation q_0 has the constant value 218 A min cm^{-3} and corresponds to the experimental electrode material mentioned above, which has volume fractions on a solid phase basis of 0·86 Cd and 0·14 $\mathrm{Fe_2O_3}$.

The interval is not specified for the electrode thickness as it is of primary interest to find thicknesses which give minimum polarizations.

3. Formulation of problems

Three problems representative of the local analysis are dealt with here. *Problem I*: Determine the capacity Q(a) which gives the best utilization of the active material for given current load and final polarization conditions; *Problem II*: Determine the smallest capacity Q(a) for a given current load and a given limit on final time and final polarization; *Problem III*: Determine the capacity Q(b) which gives the best utilization of the active material for a given current load and final polarization conditions.

The efficiency values for the different problem basis Q(a) and Q(b) are calculated from Equations 5 and 6 which define the various efficiency measures:

$$\eta_{Q(a)} = \frac{It}{Q(a)} \tag{5}$$

$$\eta_{Q(b)} = \frac{It}{Q(b)}. \tag{6}$$

I is the constant current load per surface-unit and t is the time elapsed until the polarization has reached a selected value. In Problem II the time is also a prefixed quantity and is called final time. The method of finding solutions to the problems is based on successive variations of the variables l, ϵ, q_0 and d with selection of the best combination and with regard to the variable restrictions.

4. Evaluation of optimal solutions

4.1. *Problem I*

The evaluation of the results from variation of the variable calculations can conveniently be handled in a diagram. Fig. 3 shows a collection of virtual $\eta_{Q(a)} - Q(a)$ curves with the electrode thickness as a parameter for defined current and polarization conditions. In Fig. 3 there is also a curve drawn representing the tie line for all the maximum points connected with the different electrode thicknesses. The optimal solution to Problem I corresponds to the maximum on this latter tie-curve. The lower limit on Q(a) is alternatively determined by the maximum allowed design-porosity or by the direct influence from the final polarization condition. The latter corresponds to $\eta_{Q(a)} = 0$ for $\epsilon \leqslant \epsilon_{\max}$ and the former to $\epsilon = \epsilon_{\max}$. The upper limit is solely determined by the present polarization condition.

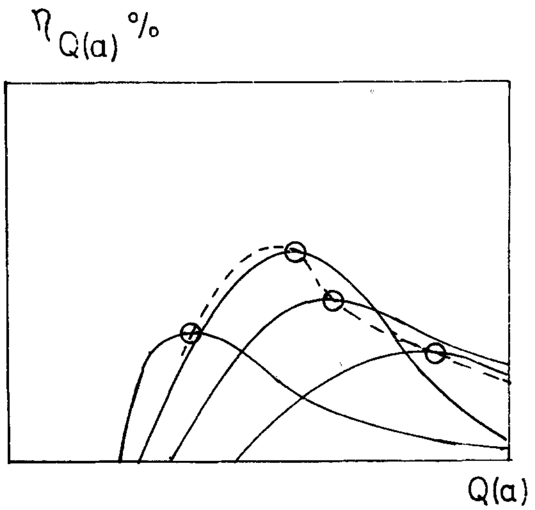

Fig. 3. The general relation between current-efficiency $\eta_{Q(a)}$ and the built-in capacity Q(a). The dotted line is the tie-line for maximum points on the $\eta_{Q(a)} - Q(a)$ curves.

4.2. *Problem II*

In order to find optimal solutions to Problem II it is convenient to extend the $\eta_{Q(a)} - Q(a)$ diagram with curves according to Equation 7

$$\eta_{Q(a)} = \frac{It}{Q(a)} = \frac{K}{Q(a)}. \tag{7}$$

In Equation 7, the constant K is characteristic for the constant current load I and the fixed final time t, for which the minimization of Q(a) is performed.

Hyperbolas according to Equation 7 are introduced in Fig. 5. The intersections between the hyperbolas and the different thickness curves give values on Q(a) which satisfy the final time conditions for different electrode thicknesses. For double intersections one has to take the smallest Q(a) value to obtain a sub-optimal solution. The best solution and the solution to Problem II can be obtained from a diagram where the sub-optimal solutions for all electrode thicknesses are collected and from which the smallest Q(a) value is to be chosen.

4.3. *Problem III*

For a constant channel-width d, Q(a) and Q(b) are linearly proportional which gives similar solutions for Problems I and III. By variation of d, a number of different solutions to Problem III can be obtained and from these the best solution is to be selected. This sequence has not been carried out here, as the selection of an electrolyte channel d has also to be considered in conjunction with other effects such as variations in the electrolyte-concentration. Another way to affect Q(b) is to discretise the system volume into a number of equal parts. Each part has an electrolyte channel d which has the same measure as in the original system volume. This method of division gives reduced space for the

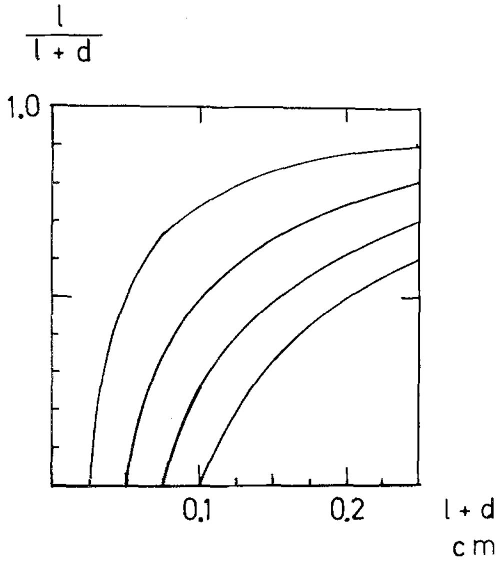

Fig. 4. The electrode volume utilization ratio $l/(l+d)$ as a function of available space, $l+d$. The different curves represent different values of d, whose values can be obtained from $l/(l+d) = 0$ co-ordinates.

active material. Fig. 4 shows the effect of the division for 1–4 sections. The effect of the introduction of electrolyte channels on the utilization of base cell volume can be extracted from the constant value, $1 + d = 0{\cdot}25$ cm. This latter value is proportional to the base cell volume. The drawback arising from reduced electrode space is logically balanced by the advantage of giving sections with lowered section current loads for a constant current load to the whole system volume. Equation 8 gives the section current density as a function of the division number N and the nominal current load I.

$$i_N = I/N. \qquad (8)$$

Sectioning as a method to obtain better electrodes has to be proved against the consequences for the counter-electrode. The latter electrode is ignored in this analysis.

If the counter-electrode is the limiting electrode, then sectioning is not an applicable method as the counter electrode will become the limiting part of the system. If the counter electrode has equal or better polarization properties, sectioning can be a valuable analytical method for the system. The usual counter-electrode to the alkaline Cd-electrode is the $NiO(OH)/Ni(OH)_2$ electrode which fulfils the condition as a better electrode at short discharge time intervals, but is the limiting electrode at deep discharges.

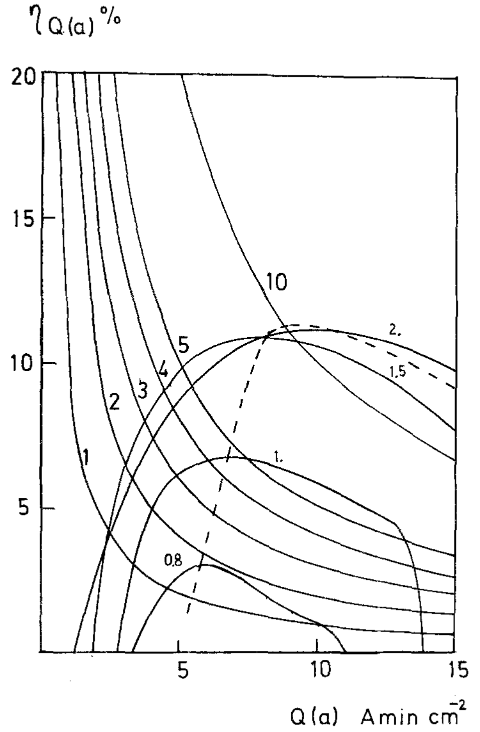

Fig. 5. Current-efficiency, $\eta_{Q(a)} - Q(a)$, curves for 100 mA cm^{-2} and 200 mV final polarization. The dotted tie-line connects different maximum points for the different parameterized electrode-thicknesses curves, 0·8, 1, 1·5 and 2 mm respectively. The parameters on the hyperbolas are given for various final times in min.

5. Results and discussion

The electrode polarizations were calculated with the numerical model described previously [1]. The calculations were made for a temperature of 22°C and the electrolyte concentration was 4·45 M KOH.

5.1. *Problem I*

Fig. 5 shows $\eta_{Q(a)} - Q(a)$ curves with the electrode thickness as parameter for 100 mA cm^{-2} and 200 mV final-polarization. The tie-curve for maximum points is given together with hyperbolas for different final time limits. On the basis of Fig. 5 it is possible to solve Problems I and II. For Problem I the best efficiency $\eta_{Q(a)}$ is obtained at 11·4%, which occurs for $Q(a) = 8{\cdot}8$ A min cm^{-2}. The corresponding optimal electrode-thickness is difficult to determine from the diagram. A simpler way of determining the thickness is to plot the maximum

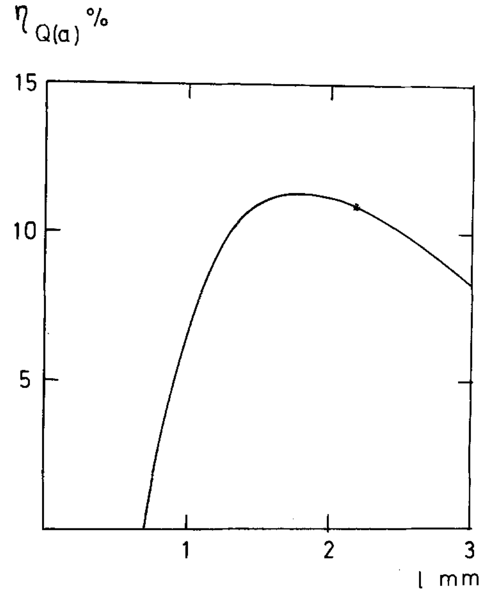

Fig. 6. The curve showing conjugated pairs of points for maximum current efficiency and electrode-thickness in connection with Fig. 5.

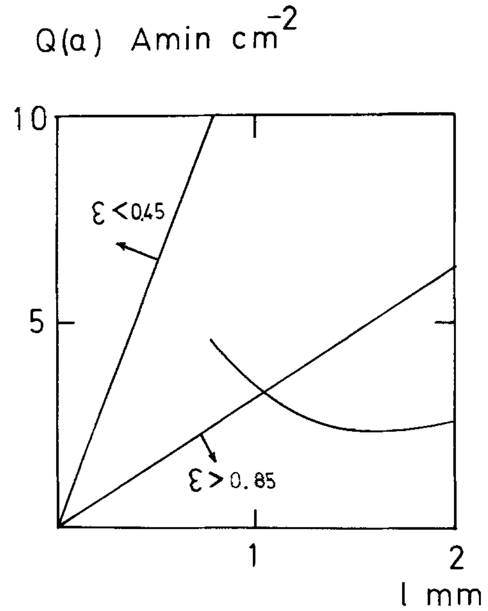

Fig. 7. The curve showing sub-optimal solutions $Q^*(a) - l$ to Problem II for 1 min final time, 100 mA cm^{-2} and 200 mV final polarization. The areas within the given porosity inequalities violate the assumed porosity restriction and represent forbidden regions of solutions.

efficiencies for all electrode-thicknesses in one diagram. Fig. 6 shows this plot of $\eta^*_{Q(a)} - l$. From Fig. 6 it can be seen that the electrode-thickness has a great influence on the efficiency; the greatest sensitivity for the electrode thickness occurs when $l < 0{\cdot}15$ cm. From Fig. 6 the electrode thickness $l = 0{\cdot}18$ cm is obtained for $\eta^*_{Q(a)} = 11{\cdot}4\%$ and this electrode thickness is the optimal one. With the known Q(a) and l, the design porosity can be calculated from Equation 3 to give $\epsilon = 0{\cdot}77$.

5.2. *Problem II*

The solution to Problem II for a specified final time can be obtained from a collection of intersections with the final-time hyperbolas and different electrode thickness curves. The intersection coordinates are conveniently plotted in a $Q(a) - l$ diagram. Fig. 7 shows $Q(a) - l$ for the final-time 1 min, 100 mA cm^{-2} and 200 mV final polarization. The smallest amount of active material is obtained as $Q(a) = 2{\cdot}3$ A min cm^{-2} which occurs for $l = 0{\cdot}17$ cm. With Equation 3, the design porosity is calculated to be $\epsilon = 0{\cdot}94$. This porosity value is outside the allowed interval. The nearest interval limit value is 0·85 which has to be chosen as the design porosity. The smallest amount of the active material and the corresponding electrode thickness can be determined from Fig. 7 as the intersection between the Equations 9 and 10:

$$Q(a) = q_0(1 - \epsilon_{\max})l \tag{9}$$

$$Q(a) = Q(a)(l, t). \tag{10}$$

Equation 9 is Equation 3 implemented with the upper-limit of porosity allowed, $\epsilon_{\max}$ and Equation 10 is the relation illustrated in Fig. 7. Equation 9 is a straight line and the area under this line contains the forbidden solutions to the problem, corresponding to $\epsilon > 0{\cdot}85$.

The intersection between the Equations 9 and 10 gives $l = 0{\cdot}104$ cm and $Q^*(a) = 3{\cdot}24$ A min cm^{-2} The optimal solution to Problem II for 1 min, 100 mA cm^{-2} and 200 mV final polarization is $Q^*(a) = 3{\cdot}24$ A min cm^{-2}, $l = 0{\cdot}104$ cm and $\epsilon = 0{\cdot}85$. From the results of Problems I and II it can be seen that they do not give identical electrode designs; which of course is the expected result from two different problem formulations. From a general point of view, Problem II is more restrictively formulated than Problem I. A direct comparison between the functions under consideration give the relations $Q^*_{\rm I}(a) > Q^*_{\rm II}(a)$ and $\eta^*_{{\rm I}Q(a)} > \eta^*_{{\rm II}Q(a)}$. The relationships show that the higher efficiency gained in Problem I is obtained through

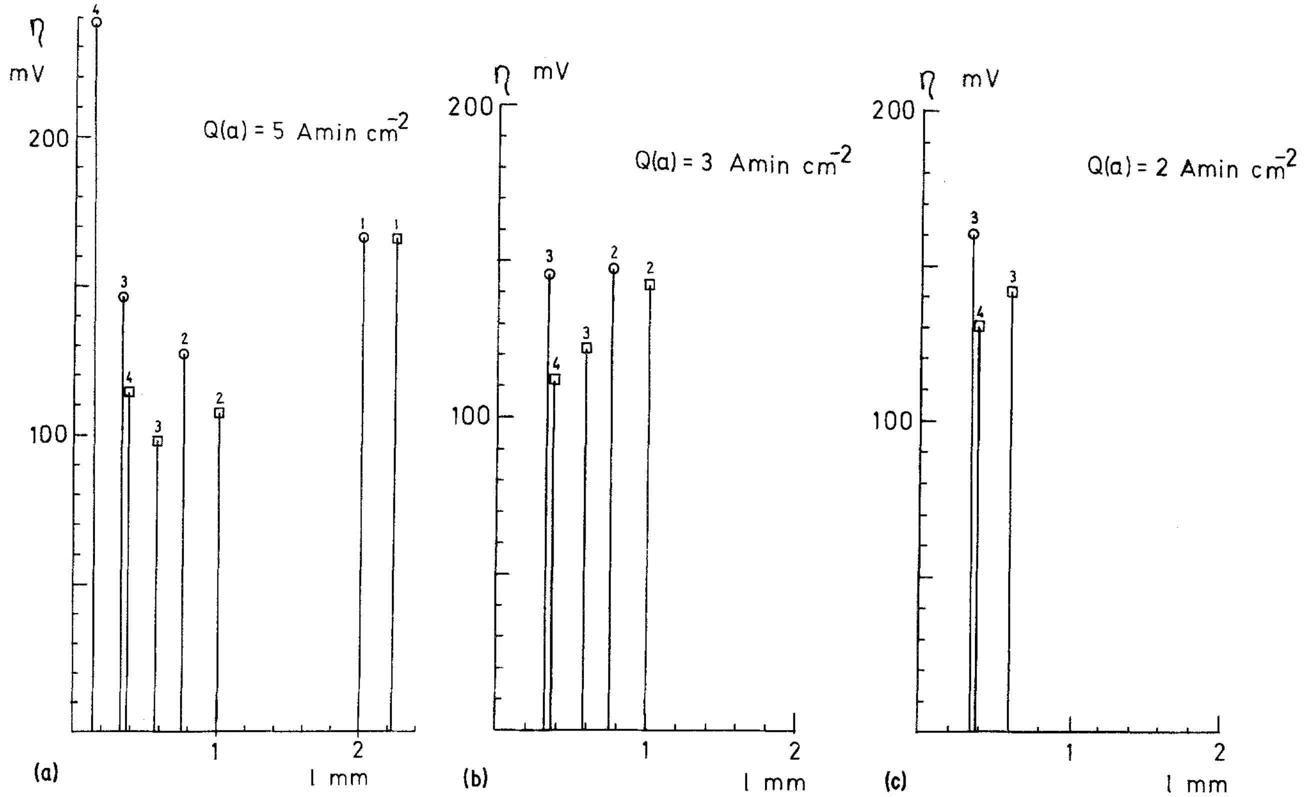

Fig. 8. Initial polarizations for sectionized electrodes for a load of 100 mA cm^{-2} to the base-volume. The symbols are, □ for 90% electrode utilization of the system volume and ○ for 80% utilization respectively ($l/(l + d)$, 0·90 and 0·80 respectively). The number on the symbols corresponds to the cell-space division numbers of the base-electrode volume. (a), (b) and (c) are for different capacities Q(a) A min cm^{-2}.

Table 1. The efficiency $\eta_{Q(a)}$ for 100 mA cm^{-2} and 200 mV final polarization

Division number N	*Volume utilization* $l/l + d$	*Capacity A min* cm^{-2} $Q(a)$	*Efficiency %* $\eta_{Q(a)}$	*Thickness cm* l	*Porosity* ϵ
4	0·90	3·0	84·8	0·0375	0·628
4	0·90	2·0	83·0	0·0375	0·750
3	0·90	3·0	63·4	0·0583	0·757
3	0·90	2·0	58·0	0·0583	0·839
3	0·80	3·0	50·6	0·0333	0·575
3	0·80	2·0	46·0	0·0333	0·718
2	0·90	5·0	36·8	0·10	0·760
2	0·80	3	30·0	0·075	0·812
1	0·80	5	8·8	0·20	0·880

The system volume $(l + d)\,1^2 = 0{\cdot}25\ cm^3$ and the spatial widths 0·05 and 0·025 cm.
N = 1, base cell.

using a greater amount of active material than is used in Problem II which produces a lower efficiency.

5.3. *Problem III*

Figs. 8a, b and c show initial time polarizations for

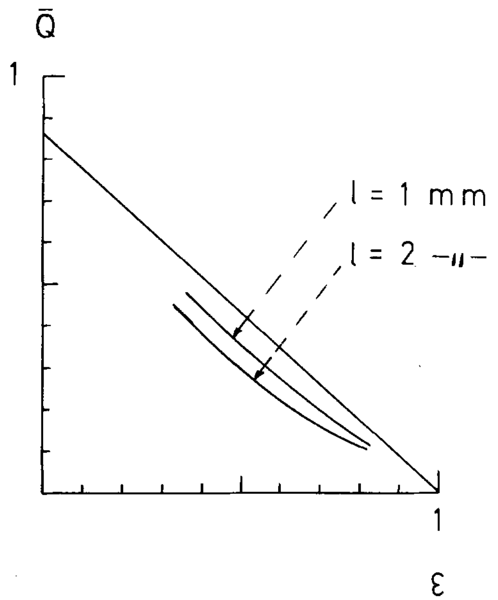

Fig. 9. A charge-porosity diagram showing calculated final porosities in the pore-mouth region for two different electrode-thicknesses. The diagram is constructed for a load of 100 mA cm^{-2} and a 200 mV final polarization. The initial states were on the full-charged line. (The diagram is presented in Reference [5]).

sectioned electrodes with constant electrode space, $l + d = 0{\cdot}25$ cm and with the channel-widths $d = 0{\cdot}05$ and $0{\cdot}025$ (including the collector). The current density for each section is calculated according to Equation 7 and for a current-load of 100 mA cm^{-2} on the base-cell. Fig. 8a shows for $Q(\mathrm{a}) = 5$ A min cm^{-2} the existence of the best division of the base-space and how this is dependent on the electrode space utilization, $l/(l+d)$. For a space utilization of 90% ($l/(l+d) = 0{\cdot}90$), $N = 3$ is the best division and for 80%, $N = 2$ is the best. Commercial high-rate electrodes have a volume utilization around 70–80%, and with half-channel-widths of about $d = 0{\cdot}05$ cm and electrode-space $l + d = 0{\cdot}25$ cm. Table 1 shows the current efficiencies for sectioned electrodes in the form of $\eta_{Q(\mathrm{a})}$ for a comparison with results from Problem I.

Table 1 shows that high space utilization combined with the sectioning procedure gives highly utilized electrodes in comparison with base-cell electrodes ($N = 1$). The best electrodes are very thin, and it can be difficult in practice to manufacture such electrodes and at the same time to maintain the open structure which has been one of the basic considerations in this analysis. The results illustrate the required ideal and suggest the way future work should be directed.

Fig. 9 shows some calculated porosities for 100 mA cm^{-2} and 200 mV polarization. The calculated charge-porosity (Fig. 5) indicates that macro-pore-blockage is not the limiting process at the chosen working conditions. It was reported earlier [1] that low porosity electrodes were macro-pore-blocked at the load-level of 100 mA cm^{-2}. The final polarization considered here is 200 mV and the one reported earlier was 500 mV, which explains the differences in the limiting processes.

6. Conclusion

The calculations presented here, although limited in scope, demonstrate the importance of proper formulation of optimization problems in electrode design. The analysis presented here could be extended to new and old active materials to obtain a range ensemble of efficiently characterized active materials. This ensemble would then be suitable to use in the efforts to determine the ultimate performance for porous electrodes.

References

[1] P. Selånger, *J. Appl. Electrochem.* 4 (1974) 249.
[2] S.U. Falk and A.J. Salkind, 'Alkaline Storage Batteries', p.48. Wiley (1969).
[3] J. Dunning, D.N. Bennion and J. Newman, *J. Electrochem. Soc.* **120** (1973) 906.
[4] D. Simonson, *J. Appl. Electrochem.* 3 (1973) 261.
[5] P. Selånger, *J. Appl. Electrochem.* 4 (1974) 263.