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Analysis of porous alkaline Cd-electrodes. III. The application of charge porosity diagrams in electrode design

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A simple charge-porosity diagram is presented for the rapid estimation of charge capacity in battery electrodes. Porosity changes reflect differences in mole volumes of the reactants and reaction products. Each system has a specific sensitivity to porosity changes. This diagram can be a useful tool for the assessment of mass and current transport performance of electrodes that give insoluble reaction products. Alkaline Cd, Zn and Fe electrolytes are compared.

Nomenclature

Symbols

c	electrolyte concentration mol cm^{-3}
F	the Faraday equivalent, As per mol equiv.
I	current, A
M	mole weight
$\bar{Q}$	normalized charge density, dimensionless
R	reactant balance ratio between matrix and electrolyte phases
t	time, s
V	electrode volume, cm^3
$\bar{V}$	partial mole-volumes, cm^3 mol^{-1}
(s)	solid phase
(aq)	aqueous phase

Greek

ε	porosity
ρ	density, g cm^{-3}
v	stoichiometric coefficients

Subscript

i	species i

1. Introduction

For the optimization of electrode composition it is important to establish the effects of the various components on the total result. The present paper gives a simple analysis based on stoichiometry, on Faraday's law and on differences in mole volumes of the different materials used in order to show some fundamental relations between capacity and porosity.

Many electrode systems have a simple basic structure with a solid consumable matrix phase and a liquid electrolyte phase that also functions as the conducting element and as the reactant supply. In most systems the solid phase reactants are present in great excess over the electrolyte phase reactants. Normal electrode systems thus have to rely on mass transport of reactants to maintain stoichiometry. This can be illustrated with the alkaline Cd/Cd(OH)$_2$ system (Equation 1). The theoretical equivalents in the solid phase can be compared with the liquid phase equivalents using the ratio R found from Equation 2.

$$\mathrm{Cd(s)+2OH^-(aq)\rightarrow Cd(OH)_2(s)+2e^-} \quad (1)$$

$$R=\frac{2\rho_{\mathrm{Cd}}(1-\varepsilon)}{M_{\mathrm{Cd}}C_{\mathrm{OH}^-}\varepsilon} \quad (2)$$

When $R=1$ the stoichiometry is balanced in the initial state. Equation 3 gives the porosity corresponding to the stoichiometric balance exemplified for 5 M alkaline electrolyte.

$$\varepsilon_{R=1} = \frac{1}{1+\dfrac{cM_{\mathrm{Cd}}}{2\rho_{\mathrm{Cd}}}} = \frac{1}{1+\dfrac{5\cdot10^{-3}\times112\cdot4}{2\cdot8\times64}} = 0\cdot97 \quad (3)$$

The high porosity value obtained for the Cd/Cd $(OH)_2$ case shows the importance of mass transport, for the complete consumption of electrodes of considerably lower porosities. Equation 4 relates the normalized charge capacity $\bar{Q}$ to the electrode porosity in the fully charged state.

$$\bar{Q} = 1-\varepsilon \quad (4)$$

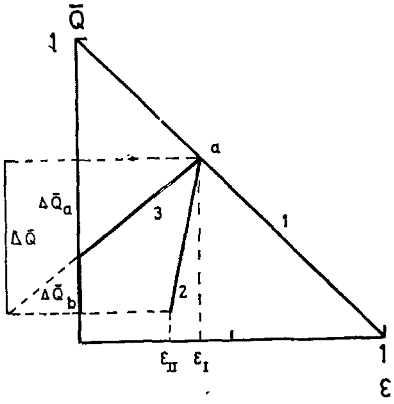

Fig. 1. Different discharge lines for a constant porosity charge change $\bar{Q}$.

2. Variations in porosity

Consider a discharge process where the solid volume of the reaction products is greater than that of the reactants. Different situations can occur depending on the initial conditions and on the magnitude of the absolute volumetric changes. In the case of a constant stoichiometric change $\Delta\bar{Q}$, there are three possibilities to be considered:

(i) a decrease in porosity
(ii) a decrease to zero porosity
(iii) a decrease to zero porosity accompanied by an increase in volume

The final state in case (i) must correspond to a higher initial porosity than that in cases (ii) and (iii). The least favourable case (ii) occurs with a fixed electrode volume with all the precipitated discharge product occupying the initial volumes of electrolyte and reacted solid matrix. Any subsequent increase in volume (case iii) is of lesser concern here and only cases (i) and (ii) need be considered.

3. The charge-state diagram

The porosity-changes can be visualized in a simple porosity-charge diagram, relating normalized charge capacity to porosity. Line 1 in Fig. 1 indicates the fully-charged state corresponding to a completely charged matrix phase. Equation 4 is the basic equation for this tie-line. The point *a* indicates the initial state, ε_I. A change in charge, $\Delta\bar{Q}$, will follow the line 2, the discharge working line, to give the final state ε_{II}. This final state will be characterized by the residual charge and a porosity $e>0$. This is case (i) with unblocked final state. In case (ii), the discharge working line, drawn from the same base point, will intersect the $\bar{Q}$-axis before reaching the theoretical total change in $\bar{Q}$. The crossing point gives the capacity at the point where the porosity disappears. Any continued change in $\bar{Q}$ beyond the crossing point will follow the zero-porosity line and will be accompanied by volume expansion (i.e. case iii). It can be shown that the distance along $\bar{Q}$, at $\varepsilon=0$, will be proportional to the volume change and is given by

$$V_{II} = \frac{\Delta\bar{Q}_a+\Delta\bar{Q}_b}{\Delta\bar{Q}_a} V_I \quad (5)$$

where the coefficient of V_I is the volume factor.

The derivative $d\bar{Q}/d\varepsilon$ is a constant for a given system when the mole volume change is linear. The three cases analysed here thus belong to different systems. Fig. 2 shows three cases for the same system when different initial porosities are taken. The lines 4 to 6 will show parallel shifts with increasing initial porosity.

Case 4 is for a high capacity system with a porosity restriction allowing only low charge withdrawal. An electrode design of this type may be appropriate for low power intensity applications. The blockage of the matrix phase, which will occur at high utilization, will not allow high mass transport from the bulk electrolyte into the electrode. Case 5 is a boundary

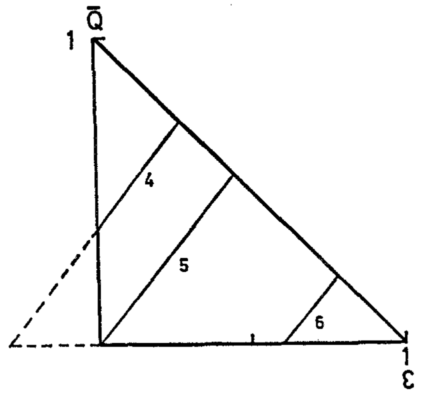

Fig. 2. Discharge lines for different initial porosities in a given system.

situation for maximum charge delivery without blockage. Here the designer will start from the origin of the diagram and draw a discharge line with the slope $d\bar{Q}/d\varepsilon$ characteristic of the system, to the full charge line. The corresponding porosity will be the lowest acceptable initial porosity. For high rate applications, case 6 applies where a high final porosity level is required in order to retain good mass transfer rates. Good transport characteristics imply inevitably that the built-in capacity will be low.

4. The effect of inert materials

Obviously, the built-in capacity will be affected by the addition of inert, passive materials. Among these will be extenders, binders and non-reacting solids added to improve conductivity.

The full charge line for a system that includes inert materials is easy to construct if the electrode composition is given on a volume fraction basis A line from the right corner ($\varepsilon = 1$, $\bar{Q} = 0$) is drawn to a point on the $\bar{Q}$-axis corresponding to the volume fraction of the active materials at zero porosity (Fig. 3). The full charge line shown in Fig. 3 for the cadmium system is for a 10% inert material content. As shown in the following section the gradient of the discharge line is not affected by the proportion of passive material.

5. The discharge line

A simple derivation of the equation for the discharge line is given here to demonstrate the properties of this line. Consider a reaction such as 1 giving a unit charge transfer of 2 F. Contributions to the volume change in the solid phase will come only from the species Cd and Cd $(OH)_2$. The volume change for a current I and a duration of Δt time units can be expressed in terms of mole volumes, $\bar{V}_i$, so that the volume change for the solid-phase, $\Delta V(s)$, will be

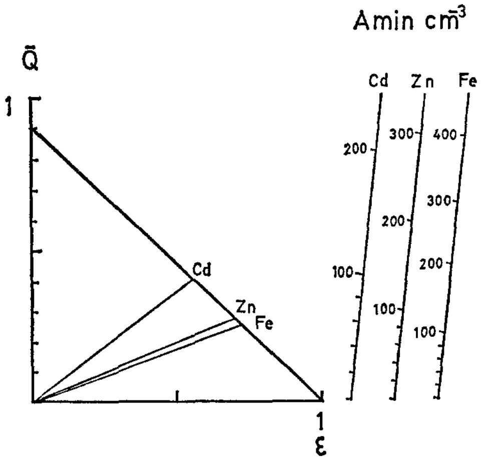

Fig. 3. Charge-porosity diagram with 10% passive material. Characteristic discharge lines are shown for $Cd|Cd(OH)_2$, $Zn|Zn(OH)_2$ and $Fe|Fe(OH)_2$ to give lowest acceptable initial porosities for high rate applications.

$$\Delta V(s) = (\bar{V}_{Cd(OH)_2} - \bar{V}_{Cd}) \frac{I\Delta t}{2F} \tag{6}$$

When related to the system volume V, this gives the porosity change,$\Delta\ \varepsilon$

$$\Delta\varepsilon = \frac{\Delta V(s)}{V} \tag{7}$$

The corresponding relative change in capacity for a quantity of charge, IΔt will be

$$\Delta\bar{Q} = \bar{V}_{Cd} \frac{I\Delta t}{2F} V^{-1} \tag{8}$$

The derivative $d\bar{Q}/d\varepsilon$ (Equation 9) can be obtained from Equations 6–8 after simplification

$$\frac{d\bar{Q}}{d\varepsilon} = \frac{\bar{V}_{Cd}}{\bar{V}_{Cd(OH)_2} - \bar{V}_{Cd}} \tag{9}$$

The discharge line for the $Cd|Cd(OH)_2$ system shown in Fig. 3, will have a gradient 0·745, when mole volumes are calculated from densities and molecular weights according to the equation.

$$\bar{V}_i = \frac{M_i}{\rho_i} \qquad (10)$$

For the general reaction (Equation 11) the discharge line can be calculated from Equation 12.

$$\nu_1 M_1(s) + \nu_2 M_2(aq) \rightarrow \nu_3 M_3(s) + \nu_3 M_4(aq) \qquad (11)$$

$$\frac{d\bar{Q}}{d\varepsilon} = \frac{\bar{V}_1}{\nu_3 \bar{V}_3 + \nu_1 \bar{V}_1} \qquad (12)$$

No change in porosity will occur when there is no net change in volume, The denominator then has value zero. This will happen when

$$\nu_3 \bar{V}_3 = -\nu_1 \bar{V}_1 \qquad (13)$$

For a dissolving electrode with soluble reaction products, $\nu_3 = 0$, the gradient will be negative, reflecting the increasing porosity. If during discharge some of the current goes into producing soluble species, the $d\bar{Q}/d\varepsilon$ curves will lose the contact with the curves based on insoluble reaction products. Zinc electrodes in concentrated hydroxide solutions can be expected to show deviations caused by the soluble zincate complex-ion $Zn(OH)_4^{2-}$. Cadmium and iron electrodes are expected to have very small deviations between the theoretical and actual $d\bar{Q}/d\varepsilon$ curves.

6. Absolute capacity

A nomogram showing the absolute charge capacity can easily be added to a normalized charge-porosity diagram by adding appropriate scales to each electrode system as shown on the right in Fig. 3 This shows absolute scales for $Cd|Cd(OH)_2$, $Zn|Zn(OH)_2$ and $Fe|Fe(OH)_2$.

From Fig. 3 it is apparent that the $Fe|Fe(OH)_2$ system is the most sensitive to porosity changes, while the $Cd|Cd(OH)_2$ system is the least sensitive to changes in capacity $\bar{Q}$. A comparison on a relative basis is somewhat misleading for practical situations as the absolute charge follows the reverse order for the metals compared here. An absolute change of 50 Amin cm^{-3} from a fully charged initial state will give final porosities of 0·30 for Cd and Zn and 0·43 for Fe. It is thus of some importance to compare different systems on an absolute scale in order to assess the porosity effects.

Acknowledgement

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