

ELECTROCHEMISTRY AND CALORIMETRY IN A PACKED-BED FLOW-THROUGH ELECTROCHEMICAL CELL

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Abstract

Packed bed electrochemical cells have come to recent prominence as a convenient way to provide a large area cathode of nickel and/or palladium, in the search for "excess heat" production. In such cells, the electrolyte is constrained to flow axially, parallel to the direction of net current flow. Calorimetry can be performed by measuring the mass flow rate and temperature rise of the electrolyte in its transit through the cell.

This paper focuses on aspects of electrochemistry, electrochemical engineering and calorimetry that are peculiar to flow-through packed-bed cells. Results will be presented of calculations intended to characterize the distribution of electrochemical process: current, potential and composition, within the heterogeneous structure of the packed bed cathode. The interpenetrating, continuous conductive elements formed by the solid phase metallic conductor (coating) and the pore-filling electrolyte phase, extended in the dimension of current flow, form a system which can be modeled as an electrochemical transmission line. The results of such modeling can be used to predict the depth of electrochemical activity within a packed bed, and to estimate the profile of hydrogen activity.

1. Introduction

By far the most effective method of assessing the distribution of process inside an extended heterogeneous electrode is by making use of the transmission line analogy. Briefly, the interpenetrating solid and electrolyte volumes of the porous electrode are replaced by their resistivities per unit length in the direction of the imposed current flux, with the interfacial impedance distributed in between. The electrode may be treated¹ as "one-dimensional" provided that quantities such as the electrical potential, V , current flux, I , and reactant concentration, c , vary only with depth within the electrode (*i.e.*, in the direction of the imposed field), and not with lateral position. The local values of V , I , and c may then be replaced by their average values in a plane perpendicular to the applied electric field gradient.

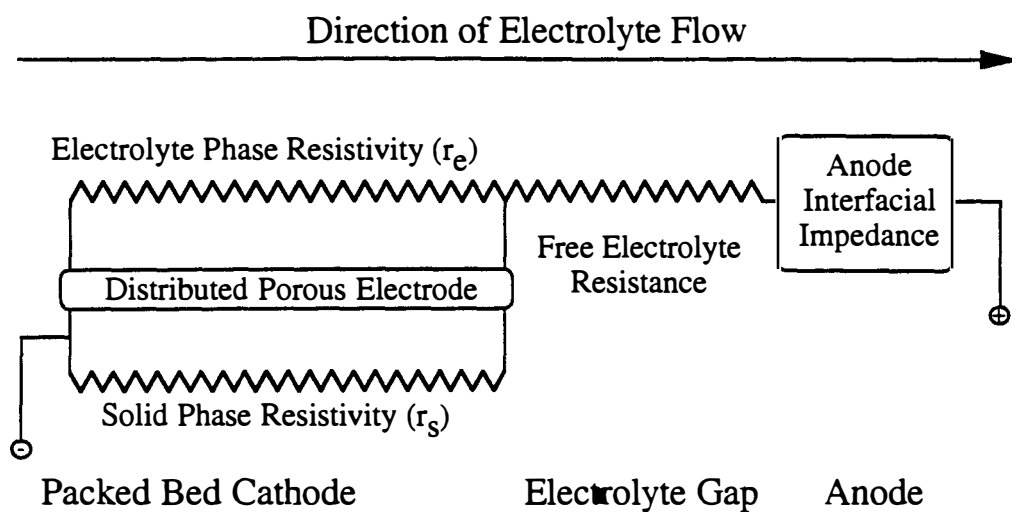
The electrode may be represented by a finite transmission line of the form shown in Figure 1. A solution to this problem was first achieved by Lord Kelvin² and has been applied widely to membrane impedance problems since 1905.³⁻⁵ Some 40 years later, this model was first used in electrochemistry by Coleman⁶ and has subsequently been extended,⁷⁻¹⁵ notably by deLevie.⁹⁻¹¹ Briefly, solutions are required to a set of differential equations of the form

$$\frac{\delta^2 I_s}{\delta x^2} + \frac{\delta \ln(1/Y)}{\delta x} \frac{\delta I_s}{\delta x} - Y (r_s + r_e) I_s = - Y r_e I \quad [1]$$

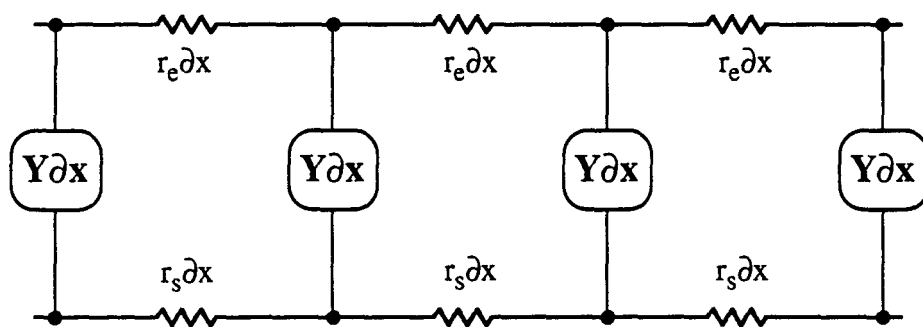
$$\frac{\delta^2 I_e}{\delta x^2} + \frac{\delta \ln(1/Y)}{\delta x} \frac{\delta I_e}{\delta x} - Y (r_s + r_e) I_e = Y r_s I \quad [2]$$

$$\frac{\delta^2 \zeta}{\delta x^2} - Y (r_s + r_e) \zeta = 0 \quad [3]$$

where subscripts e and s refer to the electrolyte and solid phases, $I = I_s + I_e$, and $\zeta = V_s - V_e$.



(a) Transmission line equivalent circuit



(b) Infinitesimally small section of the transmission line

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Figure 1 The transmission line model.

For the Patterson cell geometry shown in Figure 2, the current flows (in parallel to the electrolyte) through electrolyte and solid phase resistances that are effectively independent of the distance within the bed, x .

For this case, an analytical solution for the transmission line impedance, Z_{TL} , is easily obtained from equations [1] - [3], provided that the interfacial impedance can be considered also to be independent of x .

$$Z_{TL} = \frac{4r_s r_e + (r_s^2 + r_e^2) (e^{\gamma l} + e^{-\gamma l})}{\gamma(r_s + r_e) (e^{\gamma l} - e^{-\gamma l})} + \frac{r_s r_e l}{r_s + r_e} \quad [4]$$

where $\gamma = [Y (r_s + r_e)]^{1/2}$ and l is the bed length.

Equation [4] is an extremely powerful tool to examine, by ac means,^{14,15} the electrochemical characteristics of processes occurring within a packed-bed flow-through electrode.

The dc problem of the distribution of electrochemical activity with an extended bed electrode is more complex because of the intrinsic voltage non-linearity of electro-kinetic processes. One effective stratagem is to use a discrete transmission line model.¹³⁻¹⁵ In this approach, the continuous transmission line shown schematically in Figure 1a, comprising an infinite number of infinitesimally small sections as shown in Figure 1b, is replaced by the series sum of a (large but finite) number of segments containing discrete circuit elements of the form shown in Figure 1b. In this way we can impose an arbitrary functionality on the three elements $Y\Delta x$, $r_e\Delta x$ and $r_s\Delta x$, as these change with current density, overvoltage, composition, temperature *etc*, along the axis of the bed, x . The advantage of the discrete approach is that it allows complete generality, and the use of standard formulae for the kinetics of electrochemical processes.

2. Model Parameters

The following assumptions, constraints, dimensions and equations were used in our model calculations:

- The bed is considered to be a cylinder of radius $R = 0.75$ cm, containing 1 cm^3 of coated resin beads. The beads are modeled as a hexagonally close packed (hcp) array of monodisperse spheres of diameter 0.075 cm ($r = 0.0375$ cm). The fraction of volume occupied by hcp spheres, $\phi = 74\%$ ($= \pi/3\sqrt{2}$), and the interfacial area presented in such an array is $29.6 \text{ cm}^2 \text{ cm}^{-3}$ ($\pi/3\sqrt{2} r$), or $52.34 \text{ cm}^3 \text{ cm}^{-1}$ along the axis of the cylinder.
- The electrolyte phase resistivity is that for $1\text{M Li}_2\text{SO}_4$ at 25°C ($\rho_e = 6.7 \Omega \text{ cm}$). In the calculation we need to know the resistance per unit length, which is modified by the volume porosity (ϕ) and cross sectional area of the bed,

$$\begin{aligned} r_e &= 2 \pi R \rho_e (1 - \phi) \\ &= 14.5 \Omega \text{ cm}^{-1} \end{aligned} \quad [5]$$

- The solid phase resistivity. The flow of electrons in a "Patterson" packed bed occurs via the thin conformal metal coating on the surface of each sphere. In a well packed bed for which inter-sphere contact resistances can be neglected, we can evaluate the resistivity of a hcp array of coated spheres. by direct integration. For a coating of thickness t ,

$$\frac{\rho_{\text{hcp}}}{\rho_s} = \frac{0.89}{(q - q^2)} \quad \text{where } q = t/2r. \quad [6]$$

and

$$r_s = 1.78 \pi R / (q - q^2) \Omega \text{ cm}^{-1} \quad [7]$$

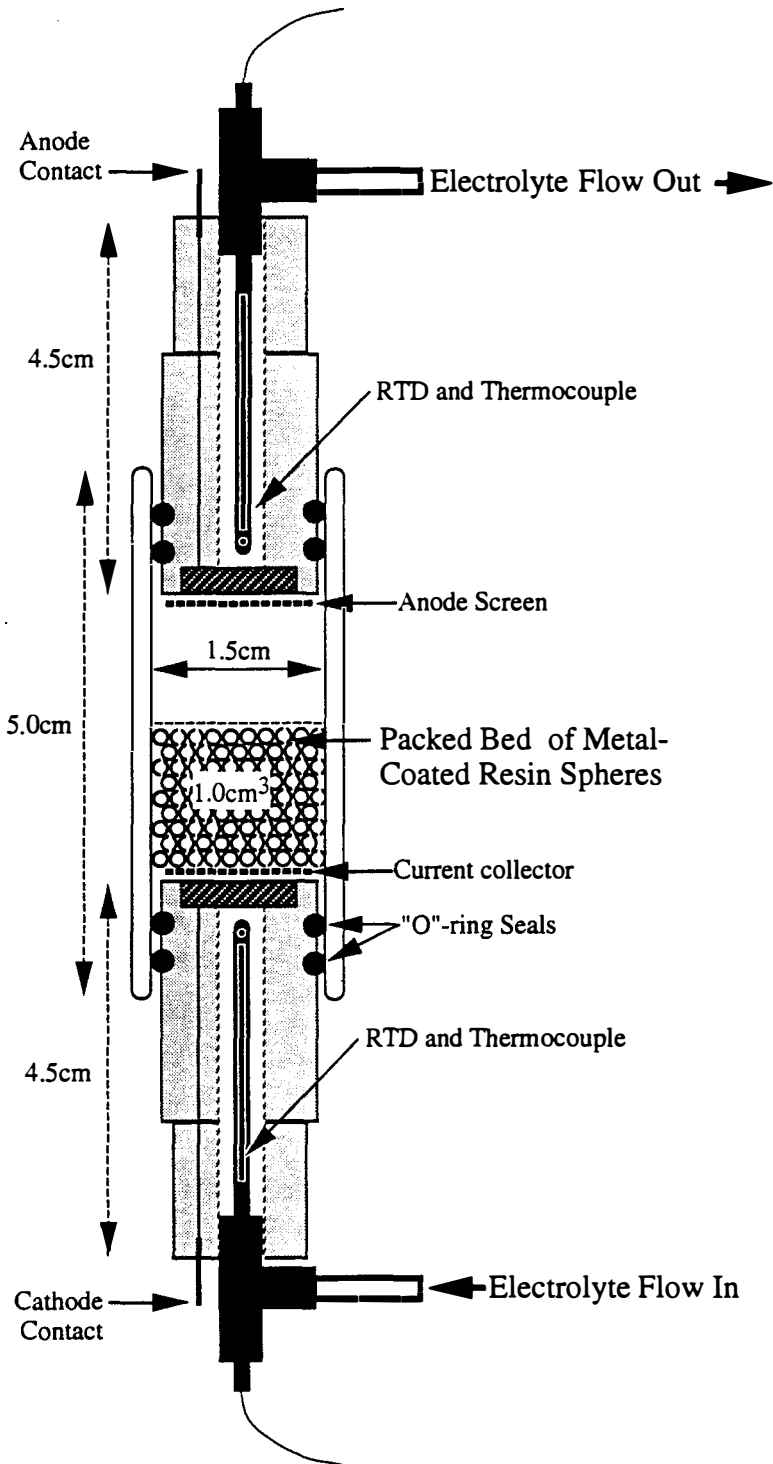


Figure 2 CETI/Patterson Packed-Bed Flow-Through Electrochemical Cell

For a coating thickness of $2 \mu\text{m}$ ($t = 2 \times 10^{-4} \text{ cm}$) of palladium and/or nickel ($\rho_s = 10^{-5} \Omega \text{ cm}$),

$$r_s = 0.034 \Omega \text{ cm}^{-1}$$

• The electrochemical process. The hydrogen evolution reaction on Group 8 metal surfaces has been studied extensively. Nevertheless the detailed mechanisms remain little understood, and the kinetics poorly quantified. The use of ac impedance measurements in association with a discrete extension of equation [4] has the potential to greatly reduce the uncertainties of electrochemical mechanisms and rates in packed bed structures. Until this is completed we have chosen to employ a simple Butler-Volmer form for the expected voltage dependence of the electrochemical process;

$$i(x) = i^\circ \{ \exp [\alpha n F \zeta(x)/RT] - \exp [(\alpha-1) n F \zeta(x)/RT] \} \quad [8]$$

where i° is the exchange current density

α is the barrier transfer coefficient

n is the number of electrons transferred

F is the Faraday constant

T is the absolute temperature

ζ is the kinetic component of the overvoltage

The use of equation [8] assumes that the hydrogen evolution rate within the bed is compositionally independent. This assumption has two parts; i° is independent of electrolyte composition, and i° is independent of the activity of hydrogen adsorbed onto the packed bed surface. In a flowing electrolyte system, and at modest or low current densities, the first assumption is likely to be valid as the electrolyte composition will change little during its transit through the bed. The effect of hydrogen atom activity on i° may require further examination and discussion.

The following values were used to calculate the results shown in Figures 3 and 4: i° was varied from 10^{-4} to $3 \times 10^{-3} \text{ A cm}^{-2}$, $\alpha = 1/2$, $n = 1$, $F = 96485 \text{ C mol}^{-1}$, and $T = 25^\circ\text{C}$ (278.15K).

3. Model Mechanics

In the transmission line model, as in the packed bed, the applied current enters the solid phase (via an appropriate current contact). At one end of the transmission line (the first element in a discrete model), all of the current is conveyed by electron motion in the solid. A local kinetic overvoltage is established between the solid and electrolyte phases which drives the electrochemical process. As a consequence of this overvoltage, an interfacial current flows between the solid and electrolyte phases such that, at the opposite end of the transmission line (the last discrete element), no current flows in the solid phase. All the current injected at one end into the solid electronic conductor, is carried at the other end by the motion of ions in the electrolyte.

Since there are no lateral leakage paths it is easy to see that the current, I , injected at one end, must flow either in the solid phase, $I_s(x)$, or in the electrolyte phase, $I_e(x)$, and nowhere else, so that these are complementary functions;

$$I = I_s(x) + I_e(x) \quad [9]$$

As these currents flow, respectively, through the solid and electrolyte phase resistances, the potentials in these phases increase due to the accumulated IR drops;

$$V_s(x) = \int_0^x I_s r_s \delta x; \quad V_e(x) = \int_0^x I_e r_e \delta x \quad [10]$$

In the discrete model, these integrals are replaced by summations.

At any position, x , the kinetic overvoltage between the solid and electrolyte phase drives the electrochemical process;

$$\zeta(x) = V_e(x) - V_s(x) \quad [11]$$

The interfacial current density is given by equation [8].

Calculations were performed using a 1000 element discrete transmission line. The current and voltage distributions in this mesh were solved using equations [8] - [11], by adjusting the local overvoltage in the first element, $\zeta(0)$, iteratively to make the solid phase current in the last element, $I_s(L) = 0$.

4. Results

Figure 3 shows the results of a series of calculations made at constant cathodic current (0.1 A), but varying exchange current density. The parameters plotted are the solid phase current, I_s , and the kinetic overvoltage, ζ , both as a function of distance, x , from the current collector at the bottom of the bed.

The current, I_s , is plotted as thinner lines referenced to the left axis of Figure 3. This current necessarily enters the bed at the imposed level, 0.1 A, and declines monotonically to zero at the top of the packed bed where free electrolyte emerges in the direction of the anode. For all cases considered, the interfacial impedance is large; that is i° is small, reflecting the known sluggish kinetics of the hydrogen evolution reaction. Because of this, the profile of $I_s(x)$ is dominated by the (relatively large) electrolyte phase resistivity, and shows little variation with i° .

The overvoltage profile exhibits a much larger dependence on the exchange current density. For large values of i° (fast kinetics) very little of the bed, and very little voltage, is needed for the imposed current to traverse the interface. At $i^\circ = 3 \text{ mA cm}^{-2}$, less than 0.2 cm of the bed can be considered to be active. At $i^\circ = 0.1 \text{ mA cm}^{-2}$, the top of the bed is approximately twice as active as the bottom, but all of the bed will be in effective operation.

5. Discussion

Considerable attention has been focused in recent years on the appearance of anomalous excess heat in Pd/D systems, and the correlation of this heat with the level of loading of deuterium into the palladium lattice.²¹ Anomalous excess heat has been reported for the Patterson cell²² as well as for other light water experiments employing palladium and nickel cathodes.^{19, 20} Very much less is known about the appearance and correlation of this thermal anomaly with proton loading, than is known from D/Pd experiments.

The direct measurement of hydrogen (or deuterium) loading in a packed bed cathode presents obvious difficulties. Nevertheless, we believe that it is important to estimate the probable distribution of this property. The following discussion which must remain speculative until further measurements are made, is an attempt to predict the distribution of hydrogen loading in a Pd coated packed bed cathode based on transmission line modeling.

We begin by noting that the loading of deuterium into palladium cathodes in alkaline environments exhibits a roughly logarithmic dependence on current density. This relationship is evident in the data of Hasegawa *et al.*,²³ from which we can deduce the following empirical relationship

$$m \approx m^* + \gamma \log_{10} (i/i^*) \quad [12]$$

where: m is the D/Pd atomic ratio; $m = m^*$ at a selected reference current, $i = i^*$; and the slope $\gamma \approx 3\%$ /decade from the Hasegawa data.

We also observe equation [12] to hold over a range of current densities, in our own experiments but we can distinguish two different modes of behavior. For electrodes that load

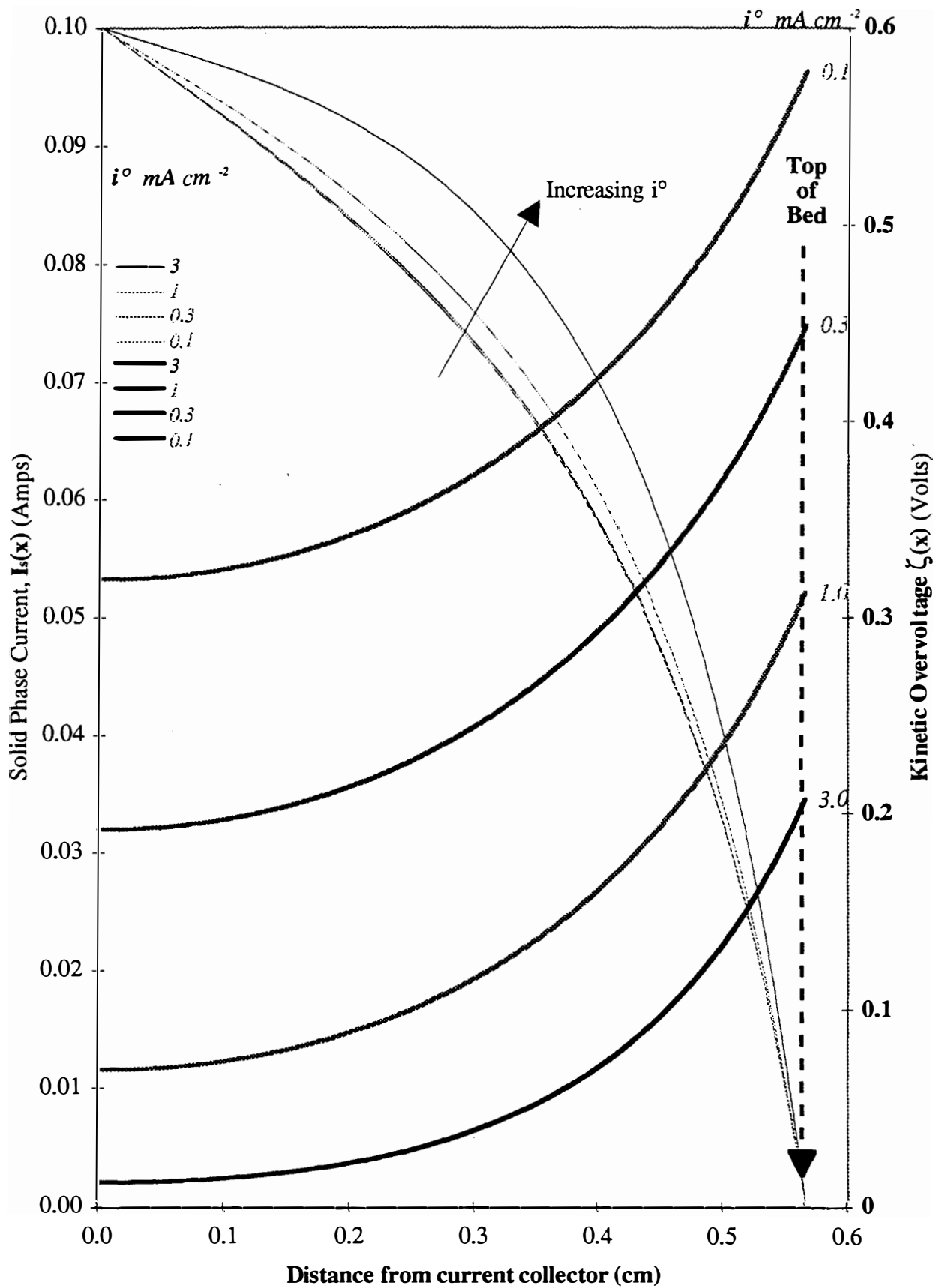


Figure 3 Distribution of Current and Voltage in a CETI Packed Bed at 0.1A cathodic.

"poorly", we measure a slope, γ , very similar to the 3% evidenced by Hasegawa.²³ For "better" loading electrodes, we see a much steeper functionality, with slope γ between 6% and 9% per decade.

Lacking further information, we make the following assumptions. That:

- i) A palladium coating behaves similarly to bulk palladium with respect to interfacial kinetics and loading characteristics.
- ii) Cathodes in light water electrolytes load similarly to those in heavy water electrolytes.
- iii) The current density/loading functionality in 1M lithium sulfate is similar to that in 1M lithium hydroxide.

If this sequence of assumption is sound then we can use equation [12] in association with the interfacial current density calculated using the transmission line model, to estimate, approximately, the loading profile in the packed bed cathode. The heavy line in Figure 4 plots the interfacial current density, $i(x)$, against distance within the bed, for one of the cases solved and presented in Figure 3 ($I = 0.1A$, $i^{\circ} = 0.001A$). This line is steeply curved, again suggesting that only the top millimeter or two of the bed show high levels of activity. Because of the logarithmic dependence with loading, however, the expected profiles of hydrogen loading are somewhat less steep. The two thin lines in Figure 4 show the profiles of loading calculated from equation [12] using two (approximately limiting) values of γ . The lower line is calculated for a value of $\gamma = 3\%$, and predicts a rather unimpressive profile of loading. The upper line, on the other hand, calculated for $\gamma = 6\%$, suggests that potentially interesting values of loading ($H/Pd \geq 0.9$) are attainable at the top of the packed bed cathode of Pd-coated spheres.

6. Summary and Conclusions

Using a discrete transmission line model, calculations were performed to estimate the profile of electrochemical parameters inside a single example of a CETI flow-through, packed-bed cathode. In this calculation the only significant uncertainty is in assigning the correct value to the interfacial exchange current density, i° . Four values were used covering the anticipated range of i° for a nickel or palladium surface coating in 1M Li_2SO_4 .

In other electrolytes, the loading of hydrogen into palladium has been observed to depend approximately logarithmically on the interfacial current density. Based on the calculated profile of this parameter, we have been able to estimate a profile for the hydrogen loading within a Pd-coated packed bed cathode. This parameter is very difficult to measure experimentally.

Based on our calculation we are able to draw the following conclusions.

- i) Calculations were performed for a relatively short bed (0.57 cm in the direction of current and electrolyte flow). This bed nevertheless exhibits a substantial dispersion of process. The end of the bed closest to the anode (furthest from the current contact) is the most active; this problem is exacerbated at high values of the exchange current density, i° .
- ii) As a corollary to (i), the packed bed structure provides a convenient means to increase the area accessed by an electrochemical process. Because of the fall-off in activity with distance from the end of the bed, however, this accessed area does not increase substantially with bed length, for lengths greater than some critical value. The bed length employed by Patterson/CETI appears well matched to the expected electrochemical characteristics.
- iii) Consistent with the assumptions used to transform the three-dimensional packed bed to its one-dimensional mathematical model, the radius of the bed is a free-scaling dimension. The accessed area can be increased without penalty, by increasing the bed radius.
- iv) Even for relatively thin metal coatings, the solid phase conductivity is much greater than that for any aqueous electrolyte. Accordingly the profile of current within the bed, and overall bed impedance, is controlled by the electrolyte phase resistivity. Increased active area can be achieved by fluidizing the bed, effectively increasing the solid phase resistivity so that it matches more closely the electrolyte phase.

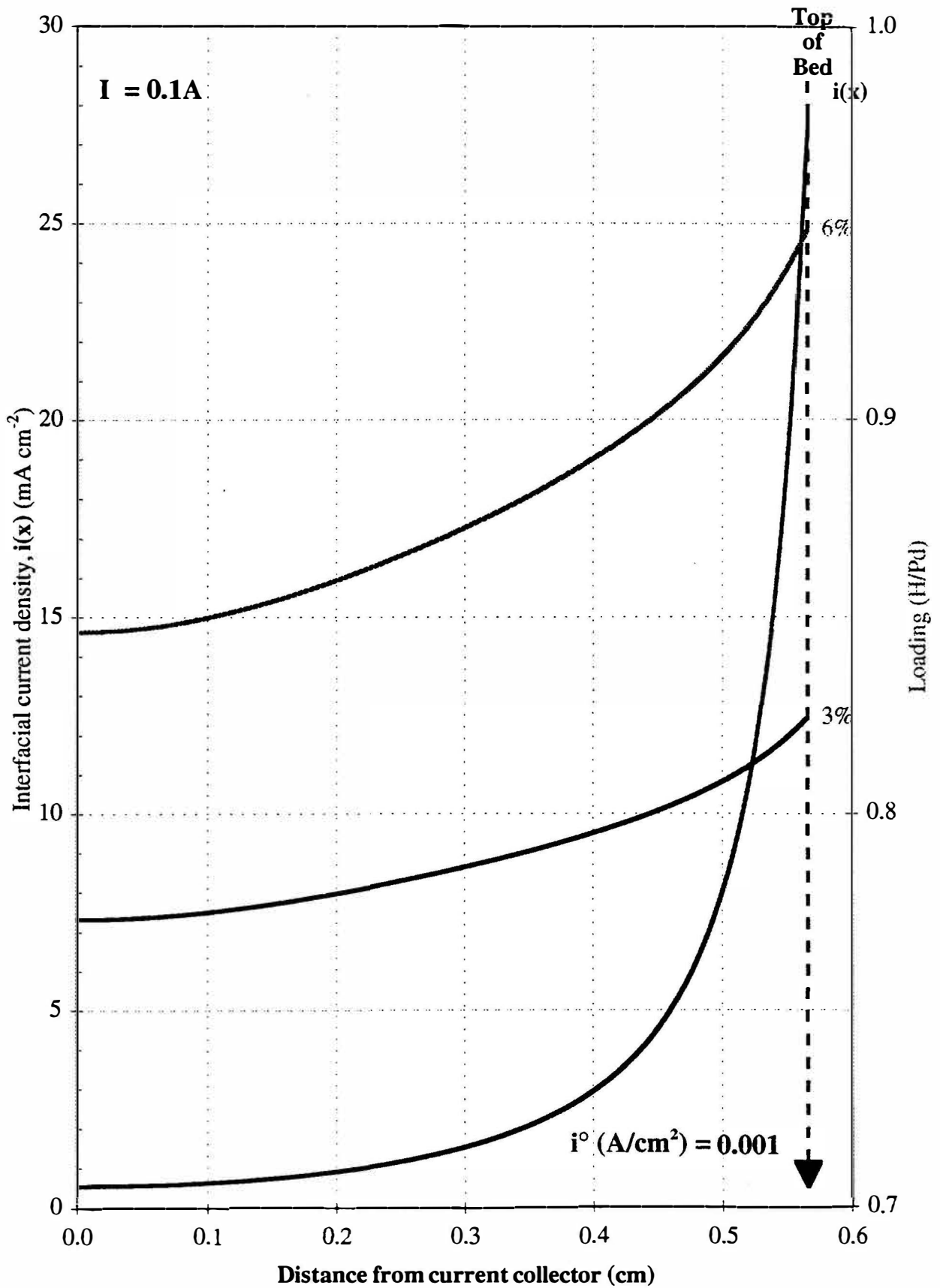


Figure 4 Distribution of Interfacial Current and Estimated Loading for a CETI Packed Bed at 0.1A Cathodic.

- v) By making some assumptions about the dependence of hydrogen loading on current density, we have estimated approximate limits for H/Pd profiles within the CETI packed bed. These profiles suggest that, for a plausible set of electrochemical parameters, modest H/Pd loadings are to be expected throughout the bed. With the most favorable loading/current density functionality, we expect intensive loading ($H/Pd \geq 0.9$) to be achieved only at the most active end of the bed.

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References

1. O. S. Ksenzheck and V. V. Stender, *Dokl. Akad. Nauk, SSSR* **106**, 487 (1976).
2. Lord (William Thompson) Kelvin, *Proc. R. Soc. (London)* **7**, 382 (1855).
3. I. G. Gurevich and V. S. Bagotskii, *Electrochim. Acta* **9**, 236 (1964).
4. L. Hermann, *Arch. Ges. Physiol.* **109**, 95 (1905).
5. G. Falk and P. Fatt, *Proc. R. Soc. (London) Ser. B* **160**, 69 (1964).
6. J. J. Coleman, *Trans. Electrochem. Soc.* **90**, 545 (1946).
7. V. S. Daniel'-Bek, *Zh. Fiz. Khim.* **20**, 567 (1946).
8. J. Euler and W. Nonnenmacher, *Electrochim. Acta* **2**, 268 (1960).
9. R. deLevie, *Electrochim. Acta* **8**, 751 (1963).
10. R. deLevie, *Electrochim. Acta* **9**, 1231 (1964).
11. R. deLevie, *Electrochim. Acta* **10**, 113 (1965).
12. G. G. Law and J. Newman, *J. Electrochem. Soc.* **126**, 2150 (1979).
13. M.C.H. McKubre, "Equilibrium and steady state studies of continuous flow-through electrode systems", report to The University, Southampton, England, 1978.
14. M.C.H. McKubre and D. D. Macdonald, "Impedance Measurements in Electrochemical Systems", in *Modern Aspects of Electrochemistry*, J. O'M. Bockris, B. E. Conway, and R. E. White, Eds., Vol. **15**, p. 61, Plenum, New York, (1982).
15. M.C.H. McKubre and D. D. Macdonald, "Electronic Instrumentation for Electrochemical Studies", in *A Comprehensive Treatise of Electrochemistry*, J. O'M. Bockris, B. E. Conway, and R. E. White, Eds., Vol. **6**, p. 1, Plenum, New York, (1984).
16. Proceedings of the First International Conference on Cold Fusion (ICCF1), National Cold Fusion Institute, Salt Lake City, UT, 1990, p. 20.
17. Proceedings of the Second International Conference on Cold Fusion (ICCF2), "The Science of Cold Fusion," Eds. T. Bressani, E. Del Giudice, and G. Preparata, Conference Proceedings Vol. **33**, Italian Physical Society, Bologna, 1992, p. 419.
18. Proceedings of the Third International Conference on Cold Fusion (ICCF3), "Frontiers of Cold Fusion", ed. H. Ikegami, Universal Academy Press, Inc., Tokyo. p. 5 (1993).
19. *Proceedings of the Fourth International Conference on Cold Fusion (ICCF4)*, EPRI TR-104188, Maui, Hawaii (1993).
20. Proceedings of the Fifth International Conference on Cold Fusion (ICCF5), Monte Carlo, Monaco (1995).
21. M. McKubre, S. Crouch-Baker, R. Rocha-Filho, S. Smedley, F. Tanzella, T. Passell, and J. Santucci "Isothermal Flow Calorimetric Investigations of the D/Pd System" *J. Electroanal. Chem.*, **368** (1994) p. 55.
22. D. Cravens "Flowing Electrolyte Calorimetry," Proceedings of the Fifth International Conference on Cold Fusion (ICCF5), Monte Carlo, Monaco (1995).
23. N. Hasegawa, N. Hayakawa, Y. Yamamoto, K. Kunitatsu (IMRA Japan Co. Ltd., Sapporo, Japan), "Observation of Excess Heat During Electrolysis of 1M LiOD in a Fuel Cell Type Closed Cell," *Proceedings of the Fourth International Conference on Cold Fusion (ICCF4)*, EPRI TR-104188, Maui, Hawaii (1993).