

Research Article

Deuterium Evolution Reaction Model and the Fleischmann–Pons Experiment

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Abstract

The hydrogen evolution reaction model was proposed many years ago by the founders of modern electrochemistry. The closely related deuterium evolution reaction model describes deuterium loading in Pd cathodes in the Fleischmann–Pons experiment. We were interested in what issues were involved in the development of a high D/Pd loading, since over the years the importance of obtaining a high D/Pd ratio to obtain excess heat has been emphasized. In order to simplify things, we focus on the Volmer and Tafel reactions, and develop a steady state adsorption isotherm for the Volmer-Tafel regime. The adsorption isotherm is extended to become an absorption isotherm within a simplified picture that takes the surface sites to be equivalent to the bulk sites. While not a particularly good approximation, this allows us to model the D/Pd loading simply as a function of the overpotential, and hence the electrochemical current density. From a Tafel curve we can get some of the parameters for the Volmer current model, and from other electrochemical data we can estimate the remaining Volmer and Tafel parameters. The resulting model fits the experimental data used well at low current density. Cathodes that load more highly with this approach require new models, potentially one for each cathode. We examine our earlier proposal that the differences in loading seen in experiment is due in part to large variations in the rate for internal D₂ leaks. Consequently, we modify the Tafel reaction current model to account for internal leaks separately from the surface gas loss, and take advantage of data from the most highly loaded cathodes to estimate the surface Tafel reaction rate. Using this approach, the reference cathode that we used for our fits initially must have an internal leak rate more than two orders of magnitude higher than the rate of surface D₂ loss. We conclude that minimizing the internal leaks is important in achieving high loading. Probably a key reason that there were so many negative results early in the field was because the cathode internal leak rate was very high in the cathodes used.

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1. Introduction

Excess heat in the Fleischmann–Pons experiment [1,2] is an effect which should not exist according to what is currently accepted in mainstream nuclear physics and condensed matter physics. We have been interested in developing a basic understanding of the experiment for many years [3]. From our perspective, part of the problem has to do with what

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kind of new physical process is involved that allows the conversion of nuclear energy to excitation in non-nuclear degrees of freedom which subsequently thermalizes; and part of the problem has to do with more conventional aspects of the problem which are amenable to analysis based on established science. In this paper our focus is on a more conventional part of the problem; in particular we are concerned with some of the the basic electrochemical issues associated with the development of high deuterium loading.

The need for high deuterium loading in Pd in the Fleischmann–Pons experiment as a prerequisite for the development of excess heat was recognized by Fleischmann and Pons (although one might take exception to the discussion of a chemical potential as high as 0.8 eV, as mentioned in the opening paragraphs of [1]). This requirement has been emphasized by McKubre and coworkers repeatedly over the years [4–7]. At issue then is the basic question of what is needed to obtain a high D/Pd loading ratio. A more general issue concerns how to model the deuterium loading in the Fleischmann–Pons experiment, perhaps as part of a more complete simulation of the excess heat effect model in which we are interested.

Of course, the electrochemistry associated with loading hydrogen or deuterium into Pd or other cathode metals has been of interest for decades. Early contributions to the theory and mechanisms are found in the early papers by Eyring and coworkers [8–10], and Frumkin and coworkers [11,12], and Bockris and coworkers [13–16]. Out of this early work developed models in use today, which goes by the name “hydrogen evolution reaction.” It appears to have been Bockris that first used this phrase in the literature [16,17].

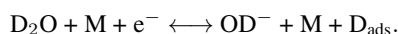
There have been a number of papers published on modeling relevant to the loading of deuterium in connection with the Fleischmann–Pons experiment [18–30]. In principle one would expect that by using the hydrogen evolution reaction model, and perhaps some account of diffusion, that all of the major issues associated with obtaining high loading in the Fleischmann–Pons experiment could be clarified. One of our goals in this discussion is to understand the relevant issues better.

2. Volmer–Tafel Regime Mechanisms

It would be possible to begin by simply implementing the hydrogen evolution equations for deuterium (in which case we would speak of the deuterium evolution equations), modeling deuterium diffusion in the cathode, and then comparing the results to experiment. We have carried out such an effort, and in the process we have understood that there are various issues that need to be addressed before such modeling is likely to be helpful and illuminating. Consequently, it will be useful to first simplify the problem, and focus on the low (cathodic) current density regime in which only the Volmer and Tafel reactions are needed (the Volmer–Tafel regime).

2.1. Basic reaction mechanisms in the Volmer–Tafel regime

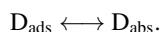
The loading of deuterium in palladium can be understood simply enough in a broad sense in terms of individual reactions that constitute the hydrogen/deuterium evolution reaction model. Deuterium is brought to the surface through the alkaline version of the Volmer reaction



Deuterium on the surface can recombine through the Tafel reaction to make D_2 gas



Adsorbed deuterium can move into the cathode to occupy more tightly bound sites associated with absorbed deuterium



Other things can happen as well (such as the Heyrovsky reaction and surface coverage by impurities). However, these basic reactions provide a simple picture which allows for a quantitative description of the cathode loading at low current density.

2.2. Loading in the Volmer–Tafel regime

In this reduced picture, the electrochemical current is dominated at the Pd surface by the Volmer reaction. When this occurs, one deuterium atom is deposited on the cathode surface as an adsorbed atom per charge transferred. In this regime, we can load the cathode simply by applying a current. As deuterium accumulates on the surface (and hence in the bulk), the deuterium chemical potential increases, making D_2 gas formation more likely. The loading is determined in the Volmer–Tafel regime by matching the incoming deuterium from the Volmer reaction to the outgoing deuterium gas associated with the Tafel reaction.

2.3. Volmer reaction kinetics model

We start with a model for the Volmer current density j_V given by [24]

$$j_V = r j_{V0} \frac{1 - \theta}{1 - \theta_0} e^{-(1-\beta_V)f\eta} e^{-\delta_V u(\theta - \theta_0)} + \text{db}, \quad (1)$$

where we follow Ref. [24] most closely. Here r is a roughness factor, θ is the fraction of available surface sites with adsorbed deuterium, β_V is an asymmetry factor, f is defined by

$$f = \frac{|e|}{k_B T} = \frac{F}{RT} \quad (2)$$

and η is the overpotential. The u parameter is a heterogeneity factor of Frumkin adsorption, and δ_V is a symmetry factor. We have included the forward (loading term) explicitly; the notation db denotes the (deloading) counter term required for detailed balance. The magnitude of the current density is determined by the parameter j_{V0} which is to be determined from experimental data taken at a loading of θ_0 .

It is worthwhile to think about this model before proceeding. We have exhibited the contribution to the Volmer current density due to the forward pathway, in which deuterium atoms are left adsorbed on the surface, which contributes to loading (and dominates over the inverse reaction under conditions of interest to us). Consequently, we expect to see a proportionality to $(1 - \theta)$, which accounts for an inability for the reaction to proceed if all the surface sites are occupied, and a reduction in the loading rate when the surface loading is already high. We recognize the exponential factors associated with statistical mechanics $\exp(\Delta G/k_B T)$ terms, one for the electron exchange ($e^{-(1-\beta_V)f\eta}$), and one for deuterium atom exchange ($e^{-\delta_V u(\theta - \theta_0)}$).

2.4. Tafel plot

We are interested in obtaining values for the fitting parameters associated with the Volmer current density. It is possible to develop an estimate for the asymmetry factor β_V from a Tafel plot. To proceed, we note that under cathodic conditions the Volmer current density is dominated by the first term so that

$$j_V \rightarrow r j_{V0} \frac{1 - \theta}{1 - \theta_0} e^{-(1-\beta_V)f\eta} e^{-\delta_V u(\theta - \theta_0)}. \quad (3)$$

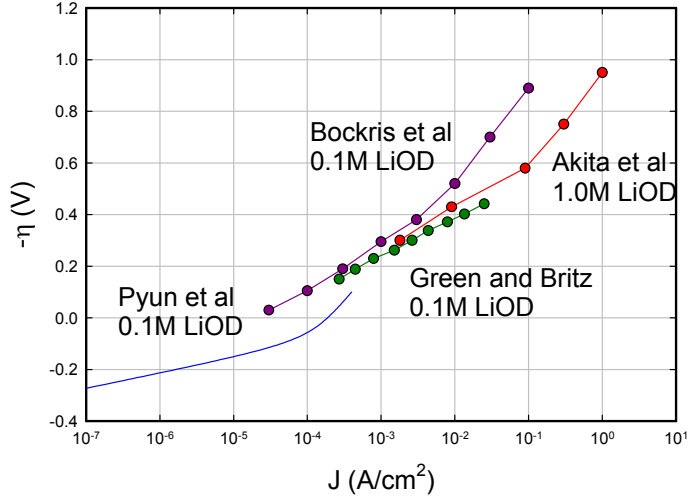


Figure 1. Tafel plots from Pyun et al. [37] (blue line); from Bockris et al. [35]; from Akita et al. [38]; and from Green and Britz [39].

This expression simplifies when we consider the special case where $\theta = \theta_0$; in this case we may write

$$j_V \rightarrow r j_{V0} e^{-(1-\beta_V)f\eta}. \quad (4)$$

At this preferred constant loading, the \ln of the Volmer current density is linear in the overpotential. From experiments it is possible to construct such a curve from measurements (a Tafel plot) and from this determine β_V and j_{V0} if r has been fixed.

In looking over the literature on Tafel plots for Pd, one finds the early papers mostly focused on Tafel plots for Pd in acid [31–33], for which the Volmer mechanism is different that discussed above. There appears to be one early paper that talks about an alkaline electrolyte [34], but the most interesting studies with alkaline electrolytes for us are much more recent [45–41]. Tafel plots from some of the experiments done in LiOD are shown in Fig. 1.

The asymmetry factor β_V can be obtained from the slope of the Tafel plot at low current density, and Green and Britz [39] give a value of 0.49 for 0.1 M LiOD; however, we will end up with better self-consistency with the simple model of the next section with a value of $\beta_V = 0.48$. For simplicity, we have adopted $r = 2$ obtained from capacitance measurements as described in this work. We are able to approximately match the data given in this paper with

$$j_{V0} = 1.70 \times 10^{-5} \text{ A/cm}^2 \quad (5)$$

and

$$\theta_0 = 0.70. \quad (6)$$

This choice in our models approximately reproduces the overpotentials that are reported in [39]. At high current density in some of the curves of Figure 1 there is a change in slope where the Volmer contribution to the electrochemical current density is no longer dominant.

2.5. Surface Tafel reaction model

In the case of the Tafel reaction, we can begin with a model for the equivalent Tafel current density j_T given by

$$j_T = r^2 j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} + \text{db}. \quad (7)$$

Here u is a Frumkin adsorption isotherm parameter [24], which takes into account the change in the chemical potential of the deuterium with loading, under conditions where the deuterium chemical potential is linear in θ . The parameter δ_T is a symmetry parameter associated with the Tafel reaction.

It is useful here to consider this parameter a bit further. For example, we might parameterize the change in Gibbs free energy associated with the transfer of a single deuterium atom in the vicinity of a reference loading ($\theta_0 = 0.70$ in this case) according to

$$\Delta G = \Delta G_0 + (\theta - \theta_0) \frac{\partial \Delta G}{\partial \theta} + \dots \quad (8)$$

If so, the associated statistical exponential factor is

$$\exp \left\{ \frac{\Delta G}{RT} \right\} \approx \exp \left\{ \frac{\Delta G_0}{RT} \right\} \exp \left\{ \frac{1}{RT} (\theta - \theta_0) \frac{\partial \Delta G}{\partial \theta} \right\}. \quad (9)$$

The zero-order term is captured within the prefactors of the model; the first order term remains explicitly, and we can identify u with

$$u = \frac{1}{RT} \frac{\partial \Delta G}{\partial \theta}. \quad (10)$$

In the beta phase, we can make use of the room temperature measurements of Chun and Ra [42], which leads to

$$u = 20.0. \quad (11)$$

2.6. Deuterium chemical potential

In connection with the estimate for the Frumkin adsorption isotherm parameter from above, it seems useful to consider the chemical potential for deuterium in Pd. The argument rests on experiments in which palladium comes into equilibrium with deuterium gas at a given temperature and pressure, and the loading is determined. In equilibrium the chemical potentials are equalized. Since the chemical potential of gas phase deuterium is known accurately, it is possible to determine the chemical potential of deuterium in PdD from such measurements.

The chemical potential of molecular D_2 satisfies

$$\frac{\mu_{D_2} + E_d}{k_B T} = -\ln z_{\text{nonideal}} - \ln z_{\text{rotvib}}, \quad (12)$$

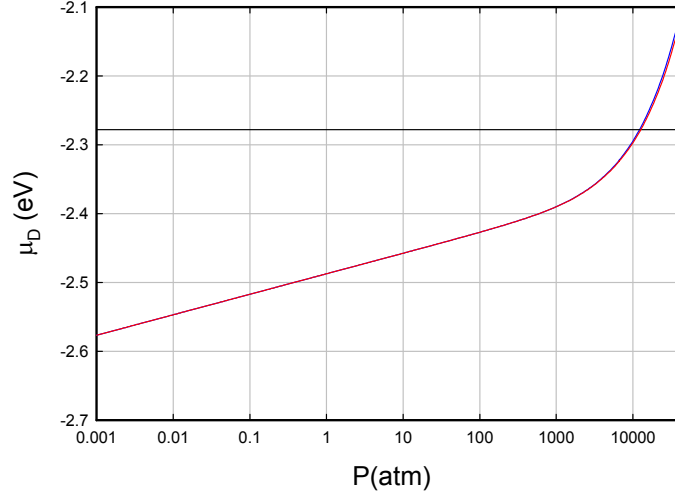


Figure 2. Deuterium chemical potential at 300 K as a function of pressure; with the D_2 fugacity from Joubert and Thiebaut [44] (red line); with the H_2 fugacity from Joubert [43] (blue line); and half the dissociation energy $-E_d/2$ (black line).

where μ_{D_2} is the chemical potential, where E_d is the dissociation energy, where z_{nonideal} is the nonideal gas partition function, and where z_{rotvib} is the rotational and vibrational partition function. For the nonideal gas partition function we may write

$$\frac{1}{z_{\text{nonideal}}} = \frac{f_{D_2}}{k_B T} \left(\frac{2\pi\hbar^2}{Mk_B T} \right)^{3/2}. \quad (13)$$

where f_{D_2} is the fugacity of D_2 gas. For the rotational and vibrational partition function we have

$$z_{\text{rot}} = 6 \sum_{\text{even } l} \sum_n (2l+1) e^{-E_{nl}/k_B T} + 3 \sum_{\text{odd } l} \sum_n (2l+1) e^{-E_{nl}/k_B T}, \quad (14)$$

where in writing this we have included the nuclear spin degeneracies explicitly.

The chemical potential for atomic deuterium in D_2 can be related to the D_2 chemical potential through

$$\mu_D = \frac{1}{2}\mu_{D_2} = -\frac{1}{2}k_B T \left(\ln z_{\text{nonideal}} + \ln z_{\text{rotvib}} \right) - \frac{E_d}{2}. \quad (15)$$

The deuterium chemical potential at 300 K is shown in Fig. 2 as a function of pressure.

We can use this to determine the chemical potential of D in PdD, by starting with the absorption isotherm for PdD. An absorption isotherm for 30°C has been constructed from data available in the literature [43–46], which is shown in Fig. 3. We can convert this isotherm from pressure to chemical potential following the discussion above to obtain an estimate for the chemical potential as a function of loading in Fig. 4. There is little difference in the chemical potential

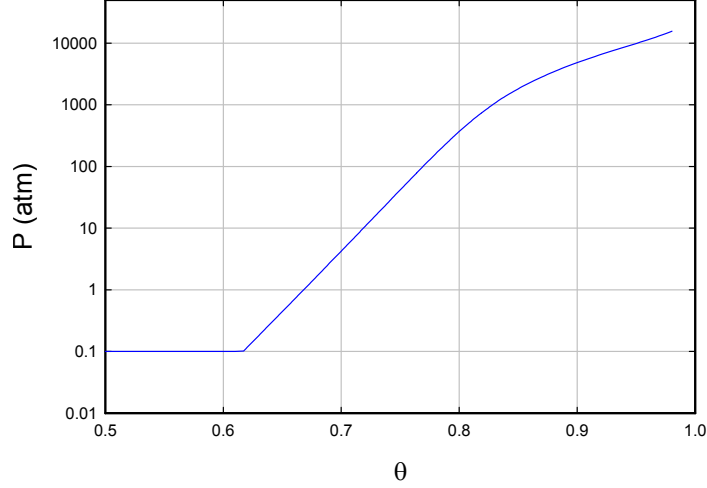


Figure 3. Absorption isotherm for deuterium in Pd at 30°C.

based on fugacity models for H_2 [43] and D_2 [44]. From this we can estimate the change in deuterium chemical potential with θ to obtain

$$\left(\frac{\partial \mu_D}{\partial \theta} \right)_T = 0.573 \text{ eV} \quad (16)$$

from a least squares fit to the data above the miscibility gap. From this we would estimate a Frumkin adsorption isotherm parameter

$$u = \frac{1}{k_B T} \left(\frac{\partial \mu_D}{\partial \theta} \right)_T = 22.2, \quad (17)$$

which is in reasonable agreement with the value $u = 20$ found from the measurements of Chun and Ra [42].

2.7. Discussion

In this section we have outlined the Volmer model for the current density associated with deuterium adsorption under cathodic conditions in an alkaline electrolyte, and the Tafel model which describes molecular D_2 formation from adsorbed deuterium atoms on the surface. From the simplest point of view, cathode loading occurs through the Volmer reaction, and de-loading occurs through the Tafel reaction, all in the Volmer–Tafel regime.

The form of the models is dictated by a combination of statistical mechanics and quantum mechanics, with empirical parameters which can be fit to model one or more cathodes. Data from a Tafel plot allows us to specify j_{V0} and β_V at a given loading θ_0 , once an estimate for the surface roughness factor is available from other measurements. The

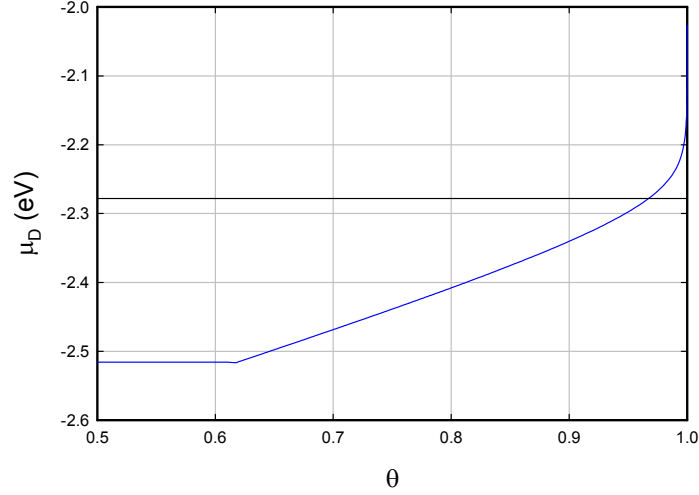


Figure 4. Deuterium chemical potential as a function of D/Pd at 30°C (blue); $-E_d/2$ (black).

model as written presumes a linear dependence of the chemical potential on the loading, which we see is approximately the case above the miscibility gap. We have an estimate for the slope from electrochemical experiments [42], and also from loading measurements of Pd in D_2 gas. We could upgrade these models by making use of the chemical potential as a function of loading with little difficulty.

It remains to determine the prefactor for the Tafel current density, and also to determine the symmetry factor associated with the chemical potential. This will require fitting to experimental loading data in the Volmer–Tafel regime.

3. Steady State Conditions and Isotherm

The models discussed above are known to be sufficient to provide a reasonable description of steady state loading at low current density. We presume in connection with this discussion that the chemical potential of the surface matches the chemical potential of the bulk in steady state, so that the surface coverage in this idealized model matches the bulk loading. We can obtain an explicit expression for the adsorption isotherm in this case, which in this simple picture gives the bulk loading as a function of the overpotential.

3.1. The Volmer–Tafel isotherm

Under steady state conditions the incoming deuterium from the Volmer reaction must be balanced by the outgoing D_2 gas from the Tafel reaction. This leads to the condition

$$j_V = j_T. \quad (18)$$

If we assume that the forward Volmer term associated with loading is dominant, and the forward Tafel term associated with deloading is dominant, then we can write

$$r j_{V0} \frac{1-\theta}{1-\theta_0} e^{-(1-\beta_V)f\eta} e^{-\delta_V u(\theta-\theta_0)} = r^2 j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)}. \quad (19)$$

It will be convenient to rewrite this isotherm as

$$\left(\frac{1-\theta}{1-\theta_0} \right) \left(\frac{\theta_0}{\theta} \right)^2 e^{-(2+\delta_V-2\delta_T)u(\theta-\theta_0)} = r \frac{j_{T0}}{j_{V0}} e^{(1-\beta_V)f\eta}. \quad (20)$$

3.2. Overpotential in steady state at $\theta = \theta_0$

At the reference loading $\theta = \theta_0$ the adsorption isotherm reduces to

$$1 = r \frac{j_{T0}}{j_{V0}} e^{(1-\beta_V)f\eta_0}, \quad (21)$$

where η_0 is defined to be the steady-state overpotential consistent with θ_0 according to Eq. (20). In the experiments described by Green and Britz [39] a loading of 0.70 for 0.1 M LiOD corresponds to about 0.6 mA/cm², and $\eta_0 = -0.15$ V at 303 K. Presumably for a different cathode in a different experiment one would obtain a different value for η_0 . We can use the adsorption isotherm at this point to develop a relation for the Tafel current prefactor

$$j_{T0} = \frac{j_{V0}}{r} e^{-(1-\beta_V)f\eta_0}. \quad (22)$$

For the parameters assembled so far we estimate

$$j_{T0} = 1.69 \times 10^{-4} \text{ A/cm}^2. \quad (23)$$

3.3. Incremental loading and incremental overpotential

Consider now the incremental change in loading for an incremental change in the overpotential. We set

$$\theta = \theta_0 + d\theta, \quad (24)$$

$$\eta = \eta_0 + d\eta, \quad (25)$$

where $d\theta$ is the incremental loading and $d\eta$ is the incremental overpotential. Around equilibrium the adsorption isotherm satisfies

$$-\left[(2 + \delta_V - 2\delta_T)u + \frac{1}{1-\theta_0} + \frac{2}{\theta_0} \right] d\theta = (1 - \beta_V) f d\eta. \quad (26)$$

From this we can write for the slope of the isotherm

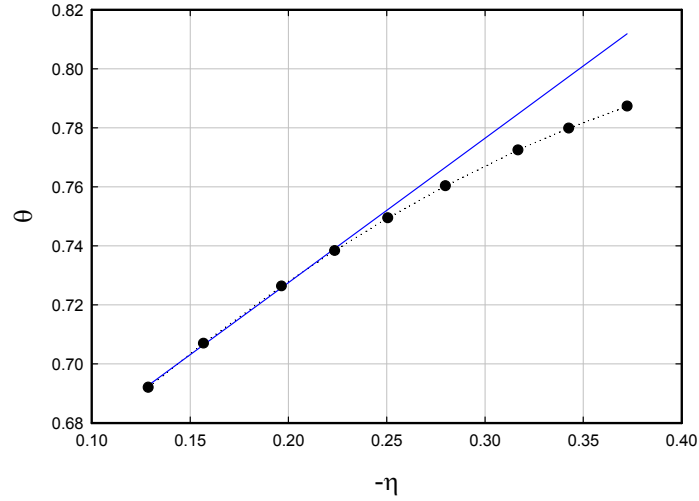


Figure 5. Loading as a function of overpotential from the data of Green and Britz [39] for 0.1 M LiOD.

$$\frac{d\theta}{d\eta} = - \frac{(1 - \beta_V)f}{(2 + \delta_V - 2\delta_T)u + \frac{1}{1 - \theta_0} + \frac{2}{\theta_0}}. \quad (27)$$

3.4. Estimation of the symmetry parameters

For loading as a function of overpotential from Green and Britz [39] for PdD in 0.1 M LiOD shown in Fig. 5 we can develop a linear fit at low loading, and hence low current density Volmer–Tafel regime of the form

$$\theta(\eta) = 0.489422(-\eta + 1.28668). \quad (28)$$

Consequently, we arrive at the constraint

$$\frac{(1 - \beta_V)f}{(2 + \delta_V - 2\delta_T)u + \frac{1}{1 - \theta_0} + \frac{2}{\theta_0}} = 0.489. \quad (29)$$

This leads to the constraint

$$\delta_V - 2\delta_T = -0.312. \quad (30)$$

Since we would like for δ_V and δ_T both to be positive, we choose

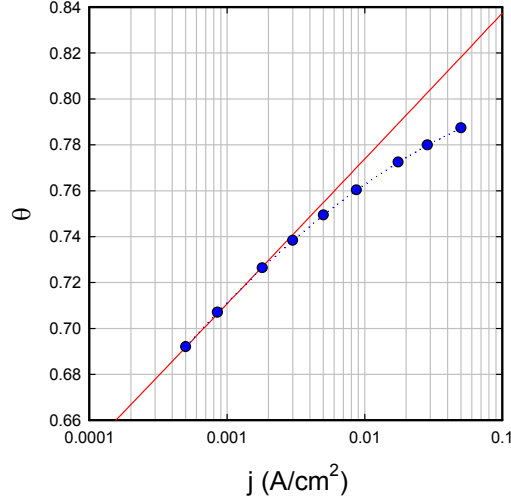


Figure 6. Loading as a function of electrochemical current density from the data of Green and Britz [39] for 0.1 M LiOD (blue circles); from the simple Volmer–Tafel isotherm of this section (red line).

$$\delta_V = 0, \quad (31)$$

$$\delta_T = 0.156. \quad (32)$$

3.5. Loading as a function of electrochemical current density

We can make use of the model parameters discussed in this section and the previous section to develop a model loading as a function of current density. The result is shown in Fig. 6 along with data points from Green and Britz [39]. One can see that the model matches experiment at low current density. At higher current density the loading is seen to be below the Volmer–Tafel regime model. This is indicative of additional processes beginning to become important at higher current density. For example, Zhang [24] discusses a model in which the Heyrovsky reaction pathway is proposed to account for the reduction of loading at higher current density. Also, Bockris proposes that the change in slope observed in the Tafel curve at high current density may be due to electrochemical desorption (Heyrovsky reaction) [40].

3.6. Discussion

We have considered perhaps the simplest possible model for the cathode loading under steady-state conditions by assuming essentially that the bulk sites are equivalent to the surface sites, and in steady state have equal occupation.

By including only the forward terms of the Volmer and Tafel current densities and setting them equal, we obtain an adsorption isotherm which is for us an absorption isotherm if bulk and surface sites are taken to be equivalent.

From matching the model to Tafel curve data, we are able to estimate β_V and j_{V0} as outlined in the previous section. From either the chemical potential as a function of loading, or from the voltametry studies of Chun and Ra [42] we have an estimate for u . From a comparison of the model with the electrochemical measurements of Green and Britz [39] we are able to develop estimates for the remaining model parameters j_{T0} , δ_V and δ_T systematically.

The basic conclusion so far is that we are able to take advantage of a subset of the deuterium evolution reaction pathways in order to develop a simple model for loading, and we are able to obtain model parameters that can be fit to experiment.

4. Modeling Cathodes with a High D/Pd Ratio

A motivation for our interest in the deuterium evolution reaction models is to understand better how loading works in the Fleischmann–Pons experiment. This is especially of interest in connection with the two loading requirements found over the years; one for a maximum achieved D/Pd loading of 0.95, and the other for a D/Pd loading greater than about 0.83 at the time excess heat is observed [4–7]. Our attention is then focused on the issue of how such high loading can be obtained. From the models discussed in the sections above we understand that deuterium is brought to the Pd cathode through the Volmer reaction, and that deuterium is lost to gas formation via the Tafel reaction. We understand that increasing the electrochemical current density is expected to produce more Volmer reactions, so that running at higher current density helps up until other processes come into play. However, we also understand that by loading we increase the chemical potential of the deuterium in the cathode, and this increases the rate at which D₂ gas leaves the cathode. In the Volmer–Tafel regime we are able to estimate the steady state loading from a balance between the two reactions.

4.1. Possible inconsistency with the model

But this is where we first run into a difficulty with the models. Our models as fit to the experimental data of Green and Britz [39] lead to an isotherm which in the complete absence of other processes predicts a maximum loading of $\theta \leq 0.84$ at 100 mA/cm². Presumably going to higher current density leads to a higher D/Pd ratio, but in the data of Green and Britz [39] we see that the increase is not going to be very much because the loading is saturating with increased current density. This effect is also seen in other experiments [38]. In essence, a version of the model that is fit to measurements on a cathode that does not load very well is going to predict a low loading in the Volmer–Tafel regime, and by extension will be inconsistent with cathodes that load more highly.

An immediate question that might be asked here is whether there are experiments in which cathodes are observed to load better? If we peruse the literature, we can find many examples where cathodes achieve higher loading [47–53]. Moreover, in some of these experiments the cathodes are observed to achieve very high loading (above 0.90) at modest electrochemical current density consistent with the Volmer–Tafel regime (under 100 mA/cm²).

4.2. Re-examination of the deuterium evolution reaction model

Consequently, this raises questions immediately about the basic deuterium evolution reaction models under discussion. If we imagined that the deuterium evolution reaction model were fundamental, then we might expect that the Volmer current model would describe the rate at which hydrogen loads through the Volmer reaction mechanism as a general statement, and similarly for the Tafel model. However, we now come to the conclusion that the models are not fundamental in this sense, simply because we need a new set of Volmer and Tafel fitting coefficients practically for

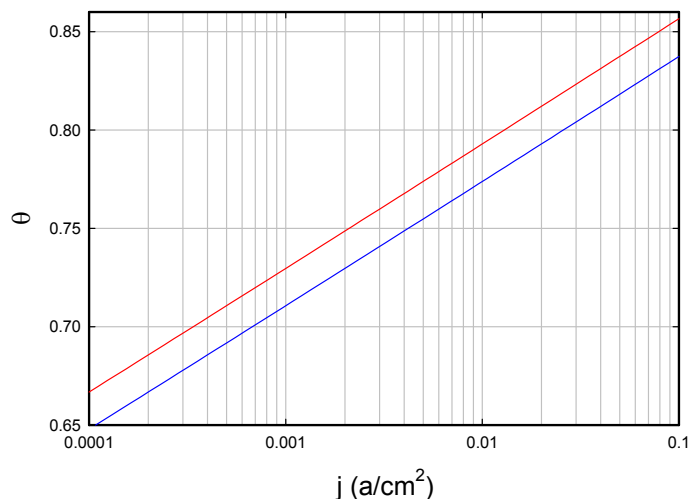


Figure 7. Volmer–Tafel isotherms for the basic model (blue line), and for a modified version of the model with a factor of 2 reduction in the Tafel prefactor (red line).

each cathode that loads to a greater or lesser degree. On the face of it this situation is either unacceptable, or perhaps much less useful than we might have hoped.

Now, we might suspect that there is a reasonably straightforward explanation for all of this. For example, it may be that at the heart of the problem is a minor variation in either the Volmer reaction prefactor (which we might explain by having either more or less active sites due to details of the surface orientation, or perhaps due to material deposited on the surface), or in the Tafel reaction prefactor (perhaps there are subtle differences in the surface which makes it either easier or harder for D_2 molecules to form).

To test this, let us consider tweaking with the Tafel prefactor in order to see how much of a difference it makes for the loading in the Volmer–Tafel regime. For example, we can imagine that one surface might have a factor of two lower Tafel current density due to some subtle surface issues that might not be obvious upon inspection. In this case, we would expect the loading to increase with less gas loss. Perhaps we can reconcile the model in this way to account for the more highly loaded cathodes. A computation of the different Volmer–Tafel absorption isotherms shown in Fig. 7 in this case shows that we only achieve a relatively minor improvement in the loading. Certainly this is not going to be sufficient to account for cathodes that load much higher.

4.3. Possibility of internal leaks

In studies that we pursued some years ago, we considered a number of different scenarios that were proposed to account for this problem. For example, if other species blocked surface sites, it is possible to reduce the Tafel current density more than the Volmer current density. However, this is not a particularly large effect unless most of the sites are blocked. Our conclusion was that if this were so, then one would see a difference in the overpotential between cathodes that load poorly and those that load well. We are not aware of such observations having been reported.

More likely in our view is a scenario in which a cathode that loads poorly does so because of internal leaks. We note that models for hydrogen and deuterium evolution are used most often in connection with cyclic voltammetry studies, in which the importance of the surface is emphasized. The use of a deuterium evolution reaction model to describe the bulk deuterium loading in steady state seems not to be so common. If we do model the bulk loading in this way, then we would naturally expect that deuterium loss through gas formation on internal surfaces would reduce the D/Pd loading. In this case we would want to modify the Tafel model to include contributions from internal leaks.

4.4. Revised Tafel model to include internal leaks

We might then generalize the Tafel model to include internal leaks according to

$$j_T = r^2 j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} + a j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} + db, \quad (33)$$

where a is the ratio of the internal surface area to the outer geometric surface area. An earlier version of this kind of model was described in [30]. Such a formulation presumes that the j_{T0} prefactor then describes D_2 gas formation as an idealized fundamental process, which acts the same (more or less) on internal surfaces as on the exterior surface. There are obvious reasons to argue that the prefactor for the internal surface could be somewhat different than for the external surface, for example due to the presence of the electrolyte on the external surface. However, our purpose here is to work with the simplest possible model that might be relevant to the problem.

4.5. Determination of model factors

To proceed we require estimates for the factors that appear in the model. Presumably j_{T0} now refers to a more fundamental Tafel surface parameter, one which we cannot readily estimate from the data of Green and Britz [39]. However, if there were a cathode known to have no internal leaks, then we could parametrize the Tafel prefactor based on electrochemical data measured with the leak-free cathode. In recent years Pd cathode fabrication was studied at ENEA, and cathodes were optimized to produce high deuterium loading. One can see in the discussion of [56] that the grain size associated with some of these very good cathodes is on the order of the foil thickness. Under these conditions, one can imagine that the internal leaks are relatively small. It would of course be possible to work with metal samples with even larger grain size; however, such cathodes do not load particularly well.

In [51] is given some results for highly loaded cathodes where the loading was determined from resistance ratio measurements tabulated with the corresponding current densities. We see a number of cathodes that achieved very high loading at modest current density, with a loading of 0.93 reported at 80 mA/cm², and 0.95 reported at 100 mA/cm². Based on this it would seem that a value of the more fundamental version of j_{T0} in the range of

$$j_{T0} = 1.0 - 1.5 \times 10^{-6} \text{ A/cm}^2 \quad (34)$$

may be consistent. In these estimates we have kept a roughness factor $r = 2$.

4.6. Internal leak rate

Once we have model parameters for the surface Tafel current, we can return to the question of the internal leak rate. For example, if we take j_{T0} to be 10^{-6} A/cm², then from the equivalent version of the fitting parameter found previously we would conclude that

$$4(1.69 \times 10^{-4}) = (4 + a)(1.0 \times 10^{-6}). \quad (35)$$

When this constraint is satisfied, the new model parameters will match our earlier fit for the Green and Britz [39] data. We can solve this to find

$$a = 672. \quad (36)$$

In light of this kind of model, we conclude that the cathode studied by Green and Britz [39] had an internal leak rate more than two orders of magnitude greater than the surface Tafel rate.

In our earlier work our estimate for δ_T was lower, and our choice for a reference cathode was one which worked better than those listed in [51]. Consequently, our estimate for the ratio of the internal leak rate to the surface leak rate here is lower than the 10^4 estimate of [30]. We would benefit in this discussion by having available systematic electrochemical data taken with a cathode that achieves very high loading. For example, with data from an appropriate reference cathode, it may be that a reduction of an additional factor of 2–5 in j_{T0} could be argued for.

5. Summary and Conclusions

Many years ago John Bockris gave some talks about the Fleischmann–Pons effect in which he emphasized the importance of the Tafel curve. The prospect that it might be possible to develop models to describe cathode loading based on a solid electrochemical model was at the time inspiring. Now roughly a quarter of a century later, we know much more about the Fleischmann–Pons experiment; however, there remain many issues that still have not been resolved. Based on the literature, and based on the discussion in the preceding sections it seems clear that we should be able to have reliable models that we can use to understand the experiment. One of the most interesting questions has always been to understand what it is that is important in obtaining high loading.

In this work our focus has been on a subset of the deuterium evolution reaction model, focusing on the alkaline version of the Volmer reaction and the Tafel reaction. In steady state, we can develop a Volmer–Tafel adsorption isotherm to describe the adsorbed deuterium fraction on the surface. Purely for simplicity we have assumed that the surface sites and bulk sites are equivalent (the energies are known to be different), which allows us to extend the adsorption isotherm to serve as an absorption isotherm within the simple picture. This is interesting, as it allows us to compute the steady state cathode loading as a function of current density in the low current density Volmer–Tafel regime, and compare with experiment.

From a comparison with experiment we can develop model parameters simply enough, and when done we end up with a reasonable match. Unfortunately this simplest version of the model does not tell us how to achieve high loading, and seemingly we require a new version of the model for each cathode we are interested in. Ultimately we concluded that the resolution to this, in light of experiments with cathodes that show very high loading, is that there are internal leaks which are important and must be included in a bulk steady state absorption isotherm model. Moreover, these internal leaks constitute the dominant loss mechanism for deuterium from the cathode. In the case of the cathode studied by Green and Britz [39] we would conclude that the rate of deuterium loss through internal leaks is more than two orders of magnitude larger than the rate of deuterium loss from surface Tafel reactions.

We recall that immediately following the 1989 announcement of Fleischmann and Pons of the observation of excess heat in their electrochemical experiments, many researchers carried out versions of the experiment in attempts to replicate the experiment. Most of these efforts did not succeed. For many years we have been interested in understanding why. By now we are very familiar with D/Pd loading requirements that have been established as a prerequisite for observing excess heat [4–7]. The question that remains is why was there so much difficulty in obtaining the high

requisite loading. It is clear from the chemical potential that it is “hard” to obtain high loading, since the chemical potential increase needed over the miscibility gap is about 250 meV. For this one needs a moderately high current density, a clean system, but perhaps most importantly the cathode needs to be free of internal leaks. We conclude that a major factor contributing to the large number of failed experiments a quarter century ago was that the cathodes simply had large internal D₂ leaks. This conclusion is consistent with a point of view advocated often by McKubre over the past quarter century.

The discussion presented here constitutes the first part of a larger study that we carried out while on sabbatical at the Naval Postgraduate School some years ago. Additional issues that we looked at include other surface reactions, deuterium diffusion within the cathode, and dynamical loading calculations to compare with dynamical experimental data. We hope to publish additional results in the coming year.

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