Electrochemical models for the Fleischmann-Pons experiment

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Abstract. The loading of Pd by hydrogen isotopes in the Fleischmann-Pons experiment does not seem to be well described by the hydrogen/deuterium evolution reaction model that is commonly used for hydrogen in metals. We consider modified versions of the model that may be more relevant to the loading of deuterium in Pd.

1. Introduction

The need for high deuterium loading in Pd in the Fleischmann-Pons experiment as a prerequisite for the development of excess heat has been emphasized by McKubre and coworkers repeatedly over the years [1-3]. We are interested in modeling the cathode loading in order to understand the associated physics, and to simulate excess heat production.

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 Volmer reaction

$$D_2O + M + e^- \leftrightarrow OD^- + M + D_{ads} \tag{1}$$

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

$$D_{ads} + D_{ads} \leftrightarrow D_2 \tag{2}$$

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

$$D_{ads} \leftrightarrow D_{abs} \tag{3}$$

Other things can happen as well (as we will discuss below). However, these three basic reactions provide a simple picture which allows for a quantitative description of the cathode loading at low current density (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.

Although there are technical issues, this simple picture can account for important features of cathode loading in the Fleischmann-Pons experiment at low current density. Unfortunately, at higher current density the situation becomes more complicated. One can find publications in the literature which make use of the hydrogen/deuterium evolution equations to describe the loading at higher current density [4,5]. Unfortunately, these models do not work particularly well when used systematically for different experiments. For example, Zhang et al [5] used such a model to account for a decrease in the loading at high current density observed in an experiment reported by Kunimatsu's group. In this model, the Heyrovsky mechanism

$$D_2O + D_{ads} + M + e^- \leftrightarrow OD^- + M + D_2 \tag{4}$$
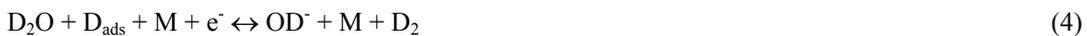
accounted for this loss of loading. The Heyrovsky mechanism decreases the loading by one deuterium per unit charge in the electrochemical current, in contrast to the Volmer mechanism that increases the loading by one deuterium per unit charge. The problem is that the kinetics rate associated with the Heyrovsky mechanism increases exponentially with loading. Hence, such a model would not predict a loading significantly higher than the maximum loading for that experiment (D/Pd of about 0.85), where there are now many reports of experiments where significantly higher loading is seen.

2. Volmer reaction kinetics model

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

$$j_V = r j_{V0} \left(\frac{1-\theta}{1-\theta_0} \right) e^{-(1-\beta_V)f\eta} + d.b. \tag{5}$$

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 $e/k_BT=F/RT$, and η is the overpotential. The notation d.b. denotes the counter term required for detailed balance. Our notation is most closely related to that of Zhang et al [5].

There are two free model parameters here (the quantity r $j_{V0}/(1-\theta_0)$, and β_V). The asymmetry factor β_V can be obtained from experiment, and we have used 0.49 as given by Green and Britz [6] for 0.1 M LiOD. For simplicity, we have adopted r=2 from this work. We are able to approximately match the data given in [6] with j_{V0} = 1.63x10^{-5} A/cm^2 and θ_0=0.70. This choice in our models approximately reproduces the overpotentials that are reported.

3. 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

$$j_T = r^2 j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2u(\theta-\theta_0)} + d.b. \tag{6}$$

Here u is a Frumkin adsorption isotherm parameter [7], which takes into account the change in the chemical potential of the deuterium with loading. In the beta phase, we have made use of the measurements of Chun and Ra [8], which leads to u = 20.0 at room temperature. In the mixed phase region below a loading of about 0.60, the chemical potential does not change with loading, so that u=0 would be appropriate. It seems that there is one remaining free parameter, j_{T0}. It is possible to obtain a reasonable fit to different data sets in the Volmer-Tafel regime, but only if we adopt a different value for j_{T0} for each experiment separately. Individual values in this case can be different by two orders of magnitude.

For the purposes of model development here, we will adopt the point of view that the reason for this variation is that there are internal surfaces where deuterium gas can evolve via the Tafel reaction, and that this gas can subsequently find its way to the outer surface. This point of view is discussed by Storms [9]. To implement this, we will augment the Tafel reaction to read

$$j_T = r^2 \left[1 + a(\theta) \right] j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2u(\theta-\theta_0)} + d.b. \tag{7}$$

where $a(\theta)$ is the ratio of the square of the internal surface area to the square of the outer geometrical surface area. In anticipation of arguments to follow, we assume that the amount of internal surface area depends on the loading.

While such a model seems to allow for a description of the effect, there is the problem that to determine j_{TO}, we require experiments carried out on cathodes that we know have no internal leaks at low loading. In this respect we draw attention to a set of experiments reported by Green and Quickenden [10] where the cathode loading was found to increase up to 0.93 for cathodes that were vacuum annealed and then etched in acid. Within the framework of the model, this pre-treatment produced a smaller value for the internal surface area. In recent experiment at ENEA Frascati with thin foils (which initially are single crystals transverse to the surface), D/Pd loadings above 1.0 have been obtained.

As a result, a low value of j_{T0} is probably appropriate. A value which seems to be in the right regime in this regard is 2.0×10^{-8} A/cm^2. Tafel current densities as a function of loading for different assumed internal areas are shown in Figure 1. According to this plot, the cathodes reported in Green and Britz have an internal area greater than the surface area by four orders of magnitude or so.
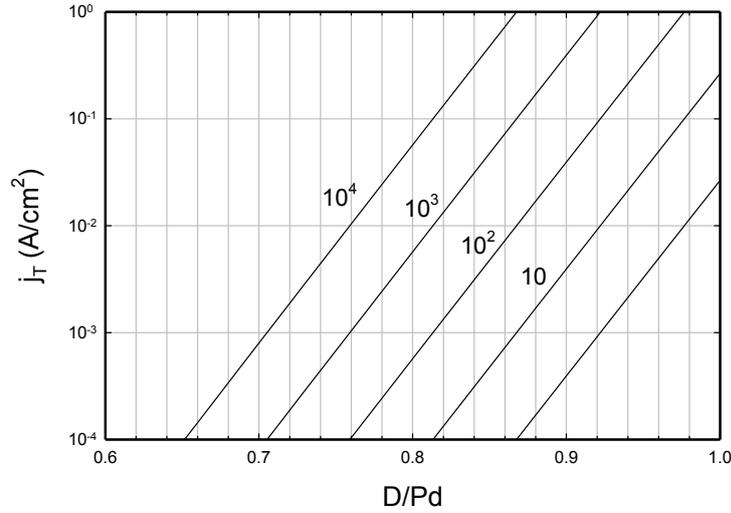

Fig. 1 – Tafel equivalent current density j_T versus loading for different values of a; the rightmost curve is for a=0.

4. Lithium model

Experiments carried out in heavy water electrolytes with LiOD show that lithium enters the cathode [11,12] in significant amounts. We assume that lithium is transported to the surface through the analog of the Volmer reaction in acid

$$Li^+ + M + e^- \leftrightarrow MLi_{ads} \tag{8}$$
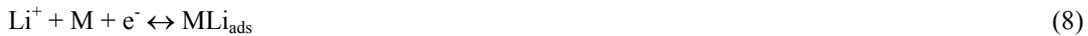
Adsorbed lithium probably comes off of the surface through a version of the lithium-water reaction

$$2Li_{ads} + 2D_2O \leftrightarrow 2LiOD + D_2 \tag{9}$$

If we assume that in steady state the adsorbed lithium is determined from a balance between these reactions, then we obtain the following adsorption isotherm

$$\frac{\theta_{Li}^2}{1-\theta-\theta_{Li}} e^{2\nu\theta_{Li}} = C\left[Li^+\right] e^{-(1-\beta_{Li})f\eta} \tag{10}$$

The measurements of the near-surface absorbed lithium concentrations of Yamazaki et al [11] can be fit well using this adsorption isotherm. The overpotentials in [11] are determined relative to a reference hydrogen electrode (RHE), which seems to give rather different results than the method used by Green and Britz [6]. If we substitute these overpotentials matching currents, then we can fit the near-surface absorption data using $\beta_{Li} = 0.53$ and $\nu = 19.4$.

5. Lattice expansion effects

As the cathode loads, the lattice constant increases. One would expect this to have an impact on the internal surface area. The loading curves of Green and Britz [6] show a reduction of loading at the higher current densities over what would be predicted from a simple Volmer-Tafel regime model (which would give the loading approximately proportional to the log of the current density). Near 0.5 mA/cm^2, the Volmer-Tafel kinetics matches the data well, but up at 50 mA/cm^2 a pronounced reduction in loading from the Volmer-Tafel model can be seen.

There is not agreement as to why the loading should decrease with increasing current density. From the discussion above, the cathode loading is determined by a balance between incoming deuterium (which is provided by the electrochemical current via the Volmer reaction) and the outgoing deuterium (which leaves as molecular D$_2$ via the Tafel reaction). As the current initially increases, there is no reason to believe that the efficiency of producing adsorbed deuterium somehow decreases (which might be the case if reactions occurred via the Heyrovsky mechanism). Measurements in this regime searching for evidence of the Heyrovsky mechanism showed that it is not present [6]. It seems unlikely that some new reaction mechanism kicks in that removes deuterium more efficiently than the Tafel mechanism.

We will assume that the loading decreases because additional internal surfaces become available as the lattice expands with increased loading. This point of view seems generally consistent with Storms [8], McKubre [10], and Zhang [13].

Once we adopt this approach, then technical questions arise as to how to implement a model which works this way. Intuitively, one would expect that the surfaces and channels that open as the lattice expands constitute physical changes in the lattice that might be expected to remain if the loading is subsequently reduced. This would show up as hysteresis in the loading curve. Although there is some hysteresis present in the loading curves, it seems that the effects are largely reversible. As such, it seems reasonable to begin with a reversible model that can sensibly be parameterized. To model the initial increase in the internal area, we have found reasonable agreement with a fit of the form

$$a(\theta) \ = \ a(0.60)\left(1+e^{w(\theta-\theta_a)^7}\right) \tag{11}$$

The idea is that the internal Tafel leak rate at the beta-phase boundary (near D/Pd=0.60), when large, dominates the loading curves in the Volmer-Tafel regime. The subsequent increase in the internal Tafel rate is then assumed to depend only on the loading, and not on the current density or overpotential. The experimental curves seem to show a similar shape that has an offset in θ. A more highly loaded cathode suffers a similar reduction in loading as compared to the Volmer-Tafel model as the loading increases. To capture this effect, we require a characteristic loading at which the increases start. This is accomplished most naturally within the model by defining a characteristic loading θ_a, which satisfies

$$\theta_a \ = \ \theta_0 + \frac{1}{2u}\ln\frac{j_{V0}}{rj_{T0}\left[1+a(0.60)\right]} \tag{12}$$

With this definition, the parameter w is fitted to be 6.0x10^5. This model seems to account well for the data of Green and Britz [6] up to 50 mA/cm^2.

5. Effects at higher current density

The model discussed above seems to be capable of extending the hydrogen/deuterium evolution reaction model to current densities up to about 50 mA/cm^2. To go higher in current density, we require further modifications of the model, for which there is even less consensus.

To proceed, we focus on three relevant experimental observations. The first is that the loading curves as a function of current density generally become flat with increasing current [9], and can show a decrease in

loading at current densities approaching 1 A/cm^2 [14]. A reversible decrease in the loading cannot be accounted for by the model above that we introduced to account for lattice expansion effects. The second observation is that the Tafel plot (overpotential as a function of current density) can show a distinct change of slope at higher current density [15]. This effect can also be seen in the data of Ref. [14]. The third observation of interest here is that the catalytic activity of Pd and other catalysts is strongly dependent on the local surface morphology, so that atoms on edges and corners are more active [16]. There is a growing literature on this issue, but we have so far not found papers yet which consider this effect specifically in the case of the Volmer reaction.

We consider first the overpotential anomaly as reported by Bockris et al [15]. In the Bockris measurement, the (negative) overpotential is seen to increase with current density at a rate of 157 mV/decade of current density between 20 μA/cm^2 and 5 mA/cm^2. At higher current density, the slope changes to 357 mV/decade. In essence, more overpotential is required to maintain the electrochemical current density. In the data of Akita et al [14], the same effect is observed, except that the slope increases near 100 mA/cm^2.

What physical process is capable of changing the slope on a Tafel plot? Usually a change of slope signals the onset of a different reaction becoming important. Such an interpretation doesn't work here because the slope increases rather than decreases. If the slope had decreased instead, then a plausible explanation is that the relative strength of a different reaction increased compared to the Volmer reaction, overtaking it at more negative overpotential where the current density is higher.

For the slope to increase, we need instead some mechanism that makes it harder to get the current to flow as the current increases. Perhaps the simplest approach is to assume that sites at which the Volmer reaction occur are getting blocked, so that more overpotential is needed to support a higher current per unit site at the remaining unblocked sites.

We can show that this approach can work in principle through a simple example. Assume that whatever blocks the active sites has an adsorption isotherm something like that of lithium given above in Equation (10). In the limit that the blocking is sufficiently efficient that most of the sites are occupied, the number of unblocked sites is exponential in the overpotential

$$1 - \theta - \theta_{Li} = \frac{\theta_{Li}^2 e^{2v\theta}}{C\left[Li^+\right]} e^{(1-\beta_{Li})f\eta} \tag{13}$$

The current density of the Volmer reaction in this limit would then acquire a different dependence on the overpotential

$$j_V = rj_{V0}\left(\frac{1-\theta-\theta_{Li}}{1-\theta_0}\right)e^{-(1-\beta_V)f\eta} \rightarrow \frac{rj_{V0}\theta_{Li}^2 e^{2v\theta}}{(1-\theta_0)C\left[Li^+\right]}e^{-(\beta_{Li}-\beta_V)f\eta} \tag{14}$$

In this limit, there will be an increased value for the change in overpotential per decade of current, as long as β_{Li} is greater than β_V. The increased slope in this model would be matched to the difference in asymmetry parameters

$$\beta_{Li} - \beta_V = \frac{\ln 10}{0.357f} = 0.167 \tag{15}$$

In our two-parameter fit of the Yamazaki data using the Green and Britz overpotential numbers, we obtained 0.53 for β_{Li}. But β_{Li} would need to be about 0.66 to be consistent with the measurements of Bockris et al given this interpretation. An approximate fit to the Yamazaki data is possible if such a large value for β_{Li} is assumed.

Now, the amount of lithium computed to be absorbed near the surface is in the few per cent range, so that we would not expect complete coverage. However, suppose that the Volmer reaction occurs primarily at edge or corner sites, and suppose further that these sites are also targets for adsorbed lithium, then this mechanism could account for the Bockris and Akita observation. If so, then the offset in current density where the slope changes could be related to the number of active Volmer sites.

There remains the question of why the loading is reduced at high current density. Given the picture above, one might conjecture that inhomogeneities are responsible for loss of loading at high current density. The basic problem with the Heyrovsky mechanism in this model is that the Heyrovsky current density has such a strong dependence on the loading. But if we assume that the loading is high close to a small number of active Volmer sites, then the local loading might be high, leading to the appearance of a Heyrovsky current density that is not connected with the average bulk loading.

6. Conclusions

We have described issues involved in the development of a new electrochemical model to describe the loading of Pd cathodes in the Fleischmann-Pons experiment. The basic hydrogen/deuterium evolution reaction kinetics model fails in this case, and we are working to develop a modified version of the model which works better. To account for the data, we have to assume that D_2 molecules are formed at internal surfaces inside that cathode. The loss of this gas is responsible according to the new model for the low loading observed in most cathodes in early experimental work. Lithium is adsorbed on the surface, and can be fit using an adsorption isotherm that results from a balance between Li^+ deposition and the lithium water reaction. The change in slope observed at high loading is attributed in the model to a blocking of a limited number of active Volmer sites by lithium (or perhaps by some other impurity that is adsorbed as a singly charged species). The decrease in loading is conjectured to be caused by a modified Heyrovsky current density that depends on local high loading near active Volmer sites. These modifications address the primary experimental issues, and it remains to develop connecting relations between the adsorbed and absorbed deuterium and lithium fractions.

7. References

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