J. Condensed Matter Nucl. Sci. 9 (2012) 10–20

Research Article

Instrumentation Relevant to Electrochemical Measurements in Condensed Matter Nuclear Reactions

John O'M Bockris *

10515 SW 55th Place, Gainesville, FL 32608, USA

Abstract

The typical electrochemical cell consists of four potentials. One of these is spurious: it should be eliminated from the measurement. A method of doing this is described. The major recommendation is that a third or, so called reference electrode, should be involved in all measurements from which structural information is to be taken from the working electrode. This is then attached to the reference electrode and a high resistance volt meter measures the potential of the working electrode with respect to the reference electrode. Alternative reference electrodes are described.
 ISSN 2227-3123

Keywords: Anode, Cells, Cathode, IR Drop, Potentiostat

1. Introduction

One of the instruments involved in investigating condensed matter nuclear reactions is the electrochemical cell. Fleischmann and Pons [1], my group of electrochemists in Texas A&M University [2], and work going on in Los Alamos National Laboratory under Ed Storms [3], were the first works to identify a specific nuclear reaction in the cold: they all used electrochemical cells.

About 100 physicists stumbled about in 1989 trying to respond to an edict put out by the head of DOE (Admiral Watkins) who told those who were interested in nuclear reactions from his department, that they should be present at a meeting in Sante Fe May 23–25, 1989 [4].

Nigel Packham, in my group at Texas A&M, was the first to report that his electrolytic vessel had given tritium in August 4, 1989 [4]. A very active group at Bhabha Atomic Research in India with more than 50 people working on it [5], also obtained tritium in 1989. Ed Storms and Carol Talcott at Los Alamos National Laboratory published a detailed study of tritium evolution in 1991 [5].

In 2011, it was discovered that Speri and Zorzi [6], two Italian engineers, had received an Italian patent for producing nuclear reactions from D which they considered was present in the hydrocarbons with which they were working (spark

*E-mail: jbockris@cox.net

 ISSN 2227-3123

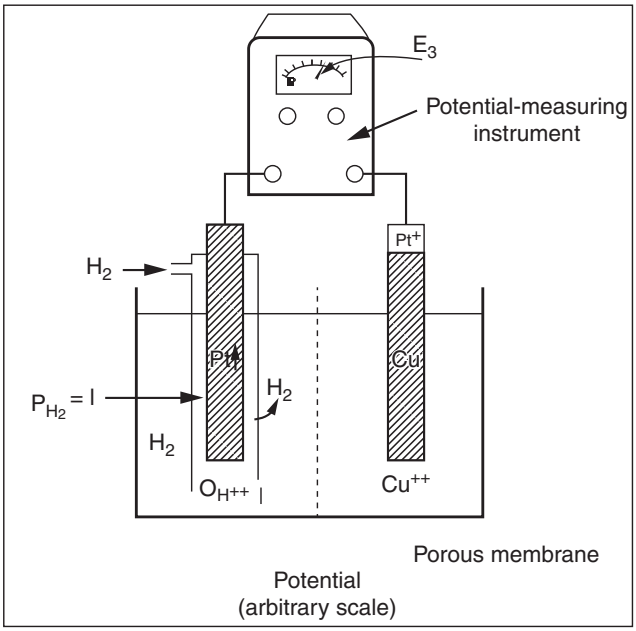

Figure 1. A galvanic cell composed of a copper electrode in cupric ion solution and a standard hydrogen electrode (a) gives a measurable potential difference E_3 (b). (From *Modern Electrochemistry,* Vol. IIA, 2000, Plenum, New York.)

effect causing explosions). Speri and Zorzi obtained a patent in 1978 for this work which was carried out in 1974. Their paper was published in 1989 in an obscure medium [7].

The objective of this paper is to present specialist information which is needed so that the electrochemical cell can be exploited to its full capacity. Other methods are available and some involve Fourier-transform, infrared spectroscopy [8] from which one may obtain information on the surface of an electrode whilst in solution. Another method which was pioneered in the Texas A&M laboratory in 1990 was the work of Marek Scklarzyck [9] who was able to observe *individual atoms* on the surface of an electrode. (Paper peer reviewed in the *J. Electrochemical Society*.)

2. The Electrochemical Cell

A basic electrochemical cell is shown in Fig. 1. On the left is what is called the "working electrode" – the electrode on which the objective of the study takes place. The solution most prevalent at this time for studies of condensed matter nuclear science was that containing lithium deuteroxide in D_2O. Whatever reaction it is wished to be carried out will be done on the "working electrode."

The cell (Fig. 1) shown is for explanatory purposes. The actual cells used by other experimentation aimed at excess heat were different than that in Figs. 1 and 2. A central electrode here was the working electrode and around it was an anode consisting of a platinum wire (see below).

Thus, on the right of the cell in Fig. 1, there is a second electrode "the counter electrode." During electrolysis with the solution as D_2O, the anode evolves oxygen.

Many using an electrochemical cell and wanting to refer to its potential take the difference between the two electrodes. However, there are two more potentials in understanding an electrochemical cell. Very often, in such cells,

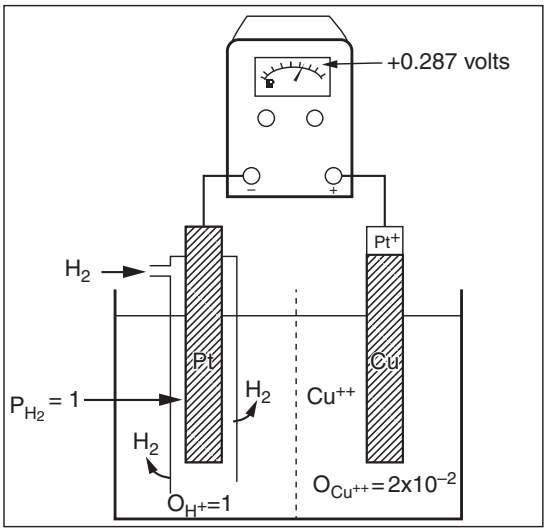

Figure 2. If the activity of cupric ions is changed, e.g., to 2×10^{-2} mol/l, the voltage of the cell should decrease to 0.287 V, as can be calculated from the Nernst equation. (From *Modern Electrochemistry*, Vpl. IIA, Plenum, 2000, New York.)

there is a different material at the cathode (left electrode) and the anode. Of course, connections to two metals must meet. When they meet, there is a contact potential generated and this is included in the potential difference between the two electrodes.

These potentials, (p.d.'s) are the basic ones which make up the cell potential and which are measured. There is a fourth potential difference which is unwanted. This potential is the so called "IR drop" between the cathode and anode (through the solution) when the cell is passing a current, this IR drop is not a valid part of the machinery which gives rise to the "cell potential." If one is to obtain the true cell potential, elimination of the IR drop is necessary. It will be dealt with in a section below although it is pertinent to say here that there are some simple methods for *reducing* the IR drop; e.g. bringing the cathode and anode as close together as possible. However, it may not contribute to the aims of the experimenter to allow the deuterium and oxygen to mix together. It is necessary sometimes to measure the deuterium and other gases which may be being produced at the cathode, without any oxygen from the anode.

In order to obtain a closer distance between the electrodes, some electrochemists use a porous membrane and then one has to judge the advantage of the nearer electrodes versus the resistance which the membrane itself brings in. Manufacturers are striving to make membranes which have a minimal resistance to the cell current.

3. Errors Made in Using Electrochemical Cells

The first and most frequent error is in reporting the data of the cell itself (Fig. 2) instead of the electrode which is evolving deuterium. The cell potential is influenced by the IR drop which should be eliminated. There are the two other potentials. One is at the junction of the anode and solution and the other potential difference is at the junction between the two electrodes of differing materials. All of these p.d.'s have to be understood in working with the cell.

Let us, for a moment, focus upon two imaginary workers: Dr. A and Dr. B are both using different electrochemical cells and examining the same reaction. Dr. A reports that his cell is working at 5.8 V (the total potential); Dr. B says his is working at 4.9 V. Comparing the current densities and the electrodes, they find they have the same current density

and yet the difference in the cell potential is relatively large – about 0.9 V. Why is that?

First of all, the IR drop can be different although the current density is the same. The distance between cathode and anode in A's and B's cells may differ. But those with experience in the use of these cells sometimes know how to diminish the IR drop. Taking this away, the two workers still find that there is a significant difference in their cell potentials. But this may be due to the materials of the anode. Some people use a platinum anode and some a nickel oxide anode or something else. Of course, Dr. A and Dr. B are measuring the cell and if different anodes are used, the whole cell will give a different potential for the same current density. Lastly, there is the contact pd between two electrodes of different materials into account.

What is the condition one needs to make if one is working with a cell? First of all, I would concentrate on the working electrode as we will see in the next section, when we see how to isolate it.

Another thing the two cells which Dr. A and Dr. B are comparing is to recall that the palladium electrodes may be indeed pure palladium 99.99%, but there is another aspect which will contribute its electrochemical properties and that is the annealing of the palladium while this is made from the liquid state. Metals cool down at different rates. This can be eliminated by letting them cool down in a temperature controlled thermostat. The vital reduction of the electrode material under cooling conditions of annealing is an important part of preparing an electrode and should be looked after if Dr. A and Dr. B want to have cells with the same performance of these cells.

Apart from this, there is the surface of the electrode which has to be prepared. It cannot be simply taken from the drawer and put into the solution. There are various methods of preparing the surfaces of the electrode which is too much detail for me to give here but it can be easily obtained [10].

Lastly, there is the question of vacancies in the electrode. Every metal has a number of vacancies which depends on this preparation and the temperature. Assuming that Dr. A and Dr. B are working at the same temperature, the annealing rate changes the number of vacancies.

4. Pitfalls of Platinum

Many electrochemical cells use a platinum counter electrode. The operator may forget that platinum has a potential at which it dissolves at potentials above 1.188 V on the hydrogen scale.

During the use of an anode in the cell, its potential may be substantially more positive so that this co-dissolution of Pt may occur. And what happens to the Pt^{++}? They diffuse over to the cathode. After this, you no longer have a palladium surface – it is of platinum.

I suspect that some people who read this will think that there are plenty of alternatives to noble metal anodes but that is not so because evolving oxygen is highly destructive. In looking for a suitable electrode which is going to be less susceptible to dissolution than platinum, it should be an oxide. The counterpoint is that most oxides do not have a large enough electronic conductivity so that they start adding to the IR drop in the cell and that is not what is wanted. Perhaps one may coat a thin layer of an oxide which isn't subject to further oxidation and does have sufficient electronic conductivity to be used without setting up a significant IR drop.

One anode worth considering is nickel oxide which I found to be a good anode but you may find something better once you look for it. Above all, it must not dissolve during anodic operation as does platinum although significantly only at higher anodic potentials.

You may wonder whether the new anode you choose is sound. That would be possible if you have a method to examine the surface of the palladium while it is in solution. I used infrared spectroscopy. The method must be usable when the solution is present. Most of the ordinary methods have to have a vacuum and the FT method will work through the solution and thus can be used but does need a fairly expensive instrument.

A cheaper method, if less informative, would be to run through an evolution of hydrogen on the palladium to see

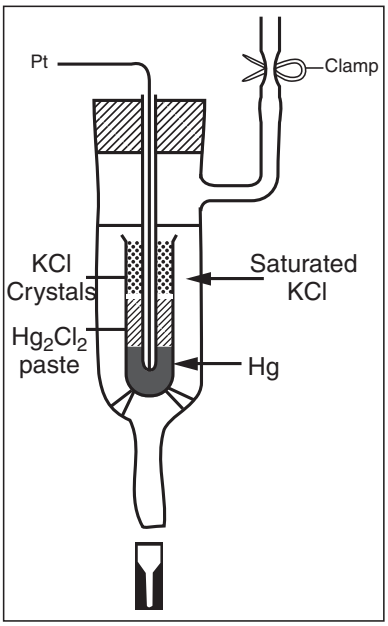

Figure 3. The calomel electrode. (One must be careful to avoid currents passing across the interface sufficient to form HgO, for this irreversibly spoils the electrode's reversible function. (From *Modern Electrochemistry,* IIA, Plenum, 2000, New York, p. 1110.)

if it fits other peoples' graphs for evolution of hydrogen on pure palladium and if it does not, then it is already coated with platinum.

5. The Isolation of the Working Electrode (See Figs. 3–5)

Some things have been explained about the properties of using an electrochemical cell. Attention should be on the working electrode as this gives the information germane to the problem. All the rest of the cell and what is happening there should be eliminated. The method involves using an auxiliary electrode – a thermodynamically reversible reference electrode.[a]

We add this small auxiliary cell (Fig. 3) which connects up the working electrode to another cell which contains a reference electrode (Figs. 3 and 4).

What thermodynamically reversible electrode should be used? Many workers would use the reversible hydrogen electrode because that is a well-known standard but it is quirky in preparation. Another reversible electrode is the calomel electrode and its potential on the standard hydrogen scale is 0.281. In this new circuit, a potentiostat is interposed (which I will describe in a separate section). A potentiostat is sensitive to the potential of the working electrode and allows the potential of this to be set and kept at the desired value during the operation of the cell. This has an advantage because from now on it is not necessary to know any more about those other potentials. The information one needs is that of the working electrode.

[a]In using any reversible electrode, the possibility of unwanted ions diffusing over from it and affecting the surface of the working electrode should be considered. If there is concern with this, a liquid junction connection can be interposed between the working electrode and reference electrode.

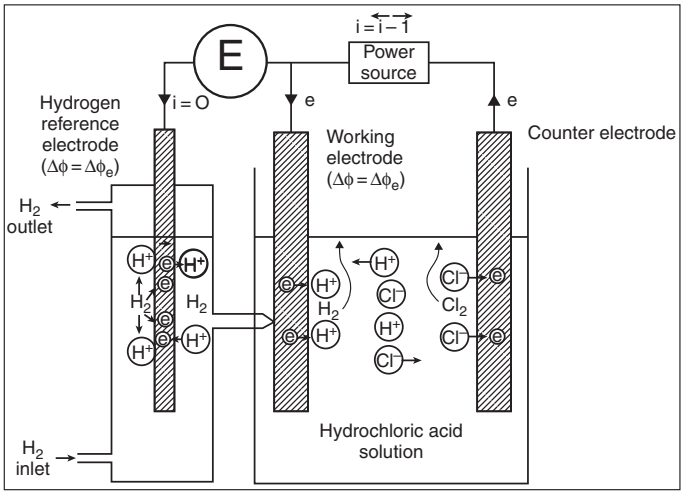

Figure 4. The three-electrode system required to measure electrode over-potentials, or use potentiostat. The potential between the working electrode and the reference electrode when both $\Delta\phi$ and $\Delta\phi_e$ correspond to the same reaction is equal to the over-potential η. The tube joining the reference electrode and the working electrode is called a Luggin capillary. It helps diminish the inclusion of an illicit IR drop in the measurement. (Reprinted from *Modern Electrochemistry*, Vol. IIA, Plenum, 2000, New York, p. 1105.)

There is an alternate reference electrode often used – the silver-silver chloride electrode. The potential of that is 0.222 on the standard H scale. These other values have to be converted to the hydrogen scale if everything else is to be measured in respect to that. But that is a matter of changing the reference electrode from whatever is being used to values for the corresponding standard hydrogen electrode (e.g., 0.222 for the silver-silver chloride reference electrode).

6. The Potensiostat

Now let us go then to the potentiostat. As the name indicates, the potentiostat keeps the *potential* of the electrode constant. The working electrode potential can be set to a given value and then some transient work which can be carried out at that constant potential. A jump up of the current is seen while the double layer is being charged and that fades away exponentially with time. It becomes a steady state potential in a short time (seconds).

How does the potentiostat work? It must be sensitive to the potential of the working electrode in order to do its job. If the potentiostat measures something too positive, the *cathodic* current is increased through the main current until the working electrode is at the desired value. Correspondingly if it is too negative, the current through the main circuit is changed until the potentiostat is at the desired value.

7. A Way towards the Elimination of IR Drops

I have referred already to the need of getting rid of IR drops, diminishing them down to 10 mV or less.

The following is a method for getting rid of all IR drops but its problem is the apparatus which is needed is not commercially available so you have to build it yourself and this can be done with minimal electronic skills.

The basis of this approach to the IR drop elimination is that the decay of the IR drop itself is very rapid (micro second) after the current through the cell has been turned off. To check my statement, one must have a quick acting measuring instrument with a micro second range and then try measuring the cell potential there with this instrument