



Research Article

# Instrumentation Relevant to Electrochemical Measurements in Condensed Matter Nuclear Reactions

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## 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.

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## 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.

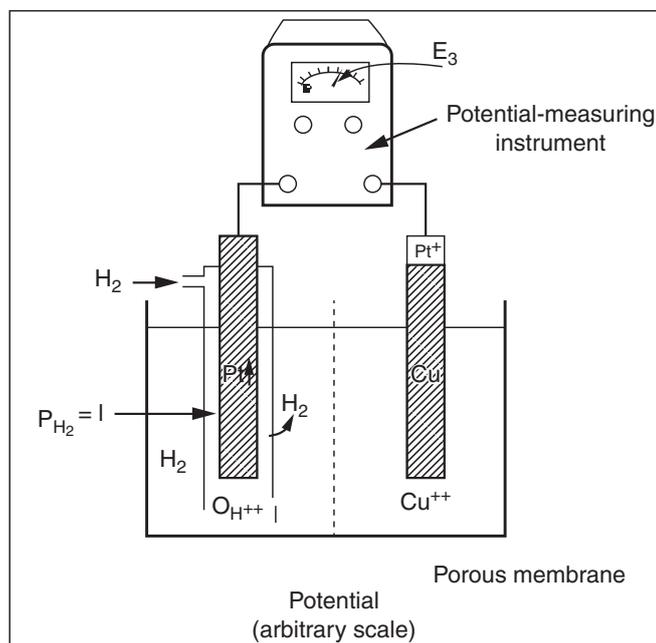
About 100 physicists stumbled about in 1989 trying to respond to an edict put out by the head of DOE (Admiral Watkins) who told those who were interested in nuclear reactions from his department, that they should be present at a meeting in Sante Fe May 23–25, 1989 [4].

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

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**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*.)

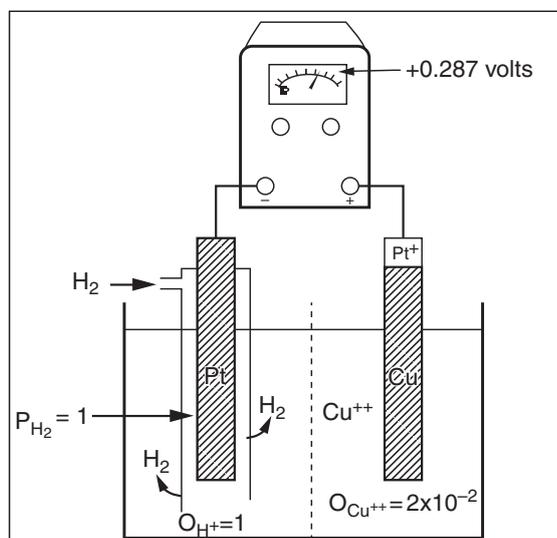
## 2. The Electrochemical Cell

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 deuterioxide in D<sub>2</sub>O. 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<sub>2</sub>O, 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  $2 \times 10^{-2}$  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.

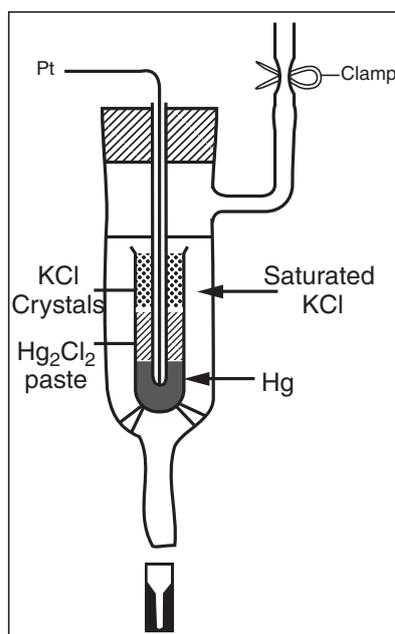
During the use of an anode in the cell, its potential may be substantially more positive so that this co-dissolution of Pt may occur. And what happens to the  $Pt^{++}$ ? They diffuse over to the cathode. After this, you no longer have a palladium surface – it is of platinum.

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  $\text{HgO}$ , 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.

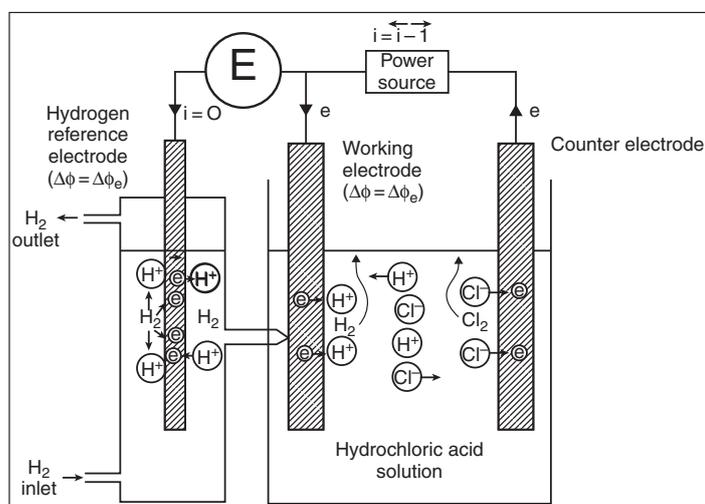
### 5. The Isolation of the Working Electrode (See Figs. 3–5)

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.<sup>a</sup>

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.

<sup>a</sup>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  $\eta$ . 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 Potentiostat

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).

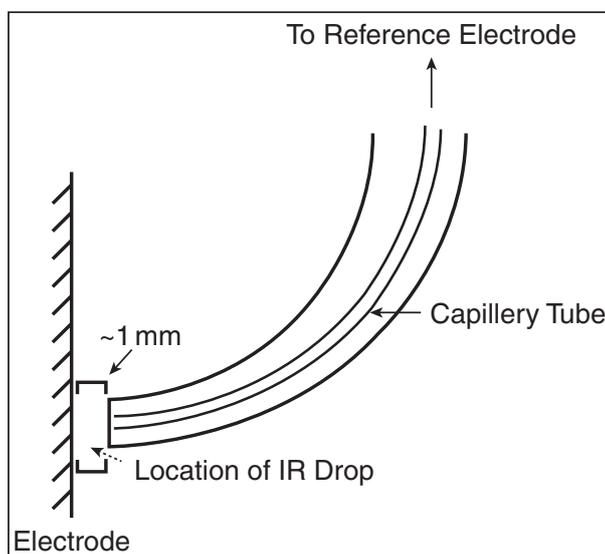
How does the potentiostat work? It must be sensitive to the potential of the working electrode in order to do its job. If the potentiostat measures something too positive, the *cathodic* current is increased through the main current until the working electrode is at the desired value. Correspondingly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



**Figure 5.** A closer look at a Luggin capillary (Reprinted from *Modern Electrochemistry*, Vol. IIA, Plenum, 2000, New York, p. 1108).

while at the same time switching off the current and you will see a rapid change of the measuring instrument showing that the IR drop has faded away in less than 10  $\mu\text{s}$ .

Now, one is interested in the potential of the working electrode. The dependence on time for this is *much slower than the IR drop*. In order of magnitude terms, the IR drop will fade away in 1 or 2  $\mu\text{s}$  and the electrode potential will remain within 10% of its original value in milliseconds. The numbers I am putting out here (1–10  $\mu\text{s}$  and a few milliseconds) will vary with the system so it would be necessary to check them out in your equipment. Important is that the IR drop decays 95% away, by the time electrode potential is switched in. The current is only off for, say, a millisecond. The cathode potential should not change more than a few percent in that time for this.

Clearly then, the measurement of the electrode potential should be done when the main current is off, no IR drop but it must be made quickly because the electrode potential also decays (but more slowly) after the current has been interrupted.

### 8. The Metal–Metal Pd (Contact Pd)

One assumes that the electrochemical potentials of the electrons are equal on both sides of the junctions:

$$\bar{\mu}_e^\alpha = \bar{\mu}_e^\beta$$

$$\mu_e^\alpha - nF\varphi^\alpha = \mu_e^\beta - nF\varphi^\beta$$

$$\varphi^\beta - \varphi^\alpha = \frac{\mu_e^\beta}{nF} - \frac{\mu_e^\alpha}{nF}$$

This is the contact p.d. between two metals at equilibrium.

If different material are being used for the cathode and the reference electrode, the metal–metal pd will be significant. Consider two metals in contact, and assume they are in equilibrium. This means then that the electrochemical potentials, a symbol for which is  $\bar{\mu}$ , are equal on both sides of the metal–metal junction.

An Individual Electrode and its Potentials [10]

The working electrode potential is shared between the metal–solution inner potential difference and the chemical potential of the electron on the phase concerned.

$${}^M \Delta^s \varphi - \frac{\mu_e^M}{nF}$$

Then, if we leave out the IR drop (see above), a whole cell, made up of the working electrode and a reversible reference electrode would look:

$$\left( {}^M \Delta^s \varphi^M - \frac{\mu_e^M}{nF} \right) - \left( {}^{\text{Rev}} \Delta^s \varphi^{\text{Ref}} - \frac{\mu_e^{\text{Ref}}}{nF} \right)$$

This is about as fundamental as one can get. Fundamental electrochemists call the  $\Delta\varphi$  term a Galvani potential difference,  $\mu$  terms refer to the chemical potential of the phase indicated.

This expression would apply to Fig. 4. This side circuit joins the reference electrode, whichever kind you choose.

There is another phenomenon which should be examined in all of these condensed matter nuclear reactions and that is the breakdown of the interior of the electrode. This has been established in recent work and may be an important aspect of what is in the future in this field [14].

One other thing I would like to draw attention to at this time and that is there is known as early as the 1960s, work done in France in which transmutation seems easy to do in bio systems and this field is now being carried out vigorously in Russia, 2010 (Vysotski and Kornilowa). These happen more easily than electrochemical transmutation reactions. This may be a future method to lead to a transmutation obtaining precious metals from those of lower costs.

## 9. Rate in Chemical Catalysis and in Electrochemistry

Current density is the current divided by the area of the electrode. In chemistry the rate of a surface reaction is measured in moles per second per unit area. The corresponding quantity in electrochemistry is:  $A \text{ cm}^2/nF$ , therefore is the same meaning if divided by  $nF$  though in a different language. So any current density one has is converted to moles per second per  $\text{cm}^{-2}$  by dividing by  $nF$  which  $n$  is the number of electrons in the act of the overall reaction;  $F$ , is 96,500 C/mol.

## 10. Some Extra Techniques may Come

In developing the instrumentation in the next twenty years, we shall be looking at surfaces in detail and I think we should be looking at atoms [9]. We already know from the work of Marek Scklarzyck carried out in my laboratory in 1990 that you can look at certain atoms on surfaces. The instrument used was a scanning tunneling microscope.

Another experiment that we should be looking at is penetration by electron microscopes into the interior of the electrode and following happenings thereon. This is because deuterium atoms not only diffuse into the palladium, but apparently damage the structure there..

## 11. Summary

Electrochemical cells were poorly understood in the early stages of work on the condensed matter nuclear reactions. Cells consist of two electrodes and their potentials must be separated. What was little realized by workers is that when

one has two different metals as a cathode and anode, the resultant metal–metal pd has to be added to the analysis of the overall cell potential. Further, there is an IR drop between the electrodes in the solution and this should be eliminated because although it is the highest and dominates the cell potential, it is of no electrochemical value. The actual cell potential excluding the IR drop, was written out in the last section.

Use of platinum in anodes may cause errors because platinum dissolves at potentials greater than 1.19 V. and deposits on the Pd electrode. NiO<sub>2</sub> or other oxides which shows sufficient electronic conductivity and stability with O<sub>2</sub> may be a substitute.

Isolation of the working electrode can be achieved by coupling it with a thermodynamically reversible electrode. The potential of the working electrode is controlled at a designed value by means of a potentiostat.

The potentiostat is a device sensitive to the potential of the working electrode. When the potentiostat registers a potential more positive than the chosen value it gives rise to a corrective change in current through the main current to bring the working electrode potential back to the original chosen value.

Potentiostats are commercially available for lab scale work. For industrial sized plants, if needed, the potentiostat has to be made to special order.

IR drops can be eliminated by using the short time in which the IR's decay compared with the much longer time for the electrode potential which can be measured up to, say, 0.1 ms.

### Acknowledgements

I am indebted to Dr. Digby MacDonald of the Pennsylvania State University for a critical reading of this document.

### Appendix A. How to Use this Paper

The use of this paper should be step by step.

- (1) The first thing would be to get rid of this IR drop, i.e., the ohmic potential which exists between electrodes in the solution.

To show you how much this can distort the answer, let me quote you a recent author who wrote to me with some details about his work. He says that the potential drop between the electrodes in his cell was about 5–6 V. After he had calculated the approximate IR drop and subtracted it, he was left at 1.5 V as the real potential between the two electrodes, leaving out the useless IR drop.

You can get within a few percent of the real answer by assuming that the passage way between the cathode and the anode is a cylinder. Now, the formula which calculates an IR drop is given by an equation:

$$R = \frac{1}{\sigma} \frac{L}{A},$$

where  $L$  is the distance between electrodes, and  $A$  the cross-sectional area between it and is the specific resistance of the solution and has to be looked up in tables and varies with the electrolyte and concentration. Finally, when one has calculated the resistance one multiplies this by the current (not the current density) and there is the IR drop which you then subtract from the reading that you are getting from the two electrodes of the cell.

It is not much use using in communication with other colleagues because there are various specific differences of people's cells which we will hear as we go through this appendix, and what I have said is the first step, and speaking numerically, is also the biggest step because the IR drop between electrodes is sometimes three-quarters of the whole potential that you are getting when you look at your high resistance volt meter.

Now, a much better method for overcoming this IR drop is quite complicated and I will delay telling you about it until we are near the end of the appendix.

- (1) After the IR drop has been removed, you still have before you the potential of the whole cell with an IR drop removed

The next thing we have to do is isolate the working electrode which if you look at the diagrams, the one on the left in Figs. 1 and 2. Thus, in order to isolate the working electrode, the main way to do it is to use a third electrode which is a thermodynamically reversible electrode at equilibrium so that no current passes in it and one knows exactly what its potential is so that if one measures the working electrode potential versus the reference electrode potential, then one is free of all IR drop and also other problems such as the fact that the anode had its own potential which you'd like to thrust aside and there is another potential when one metal touches platinum and meets another metal such as palladium, there is a p.d. set up between the two of them, and you have to reckon that one too.

- (1) Figure 5 shows the Luggin Capillary. This leads from the reversible reference electrode on the extreme left of Fig. 4 to the working electrode and the reason for having it is to avoid including a little IR drop in the solution near the working electrode
- (2) The fourth step would bring the author into the sophisticated measurement because he will be taking into account everything which gives him the information that he wants, which is the behavior of the working electrode protected from the influence of other things such as the current going over to the anode and the metal-metal p.d. which we mentioned.
- (3) If you have been through Steps 1–4, you are producing data which is worth recording in a paper because everybody's paper has different IR drops and different anodes and different metal-metal p.d.'s but if you wipe all those and look only at the potential of the working electrode, and you can compare your results with those of any other experimenter who has taken the same steps.
- (4) I strongly advise experiments which examine damage inside the electrode.

For example, in those two papers which I published, in 2000, and in 2011, we found that at 0.35 V for the over potential, there was a beginning of a breakup inside the palladium. This breakup starts the reactivity in respect to tritium which we have been trying to produce for the last 100 hours begins, i.e., no tritium for 100 h.

### List of Symbols

$\bar{\mu}^\alpha$	the electrochemical potential of the phase $\alpha$
$n$	the number of electrons which take part in the overall reaction with you are examining, e.g. = 2
$F$	96,500 C/gmol of univalent ions
$\mu^\alpha$	the chemical potential of the phase $\alpha$
$\varphi^\alpha$	the inner potential of the phase $\alpha$
${}^\alpha \Delta^s \varphi$	the inner potential difference between the bulk of the interior of the metal and the bulk of the interior of the solution

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