Full Paper

A New Overpotential — Capacitance Mechanism for H$_2$ Electrode

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Abstract: The H$_2$ electrode is commonly assumed to be a half-cell, $2 H^+ + 2e == H_2$, and explained by the Nernst equation. We cannot assume that the H$^+$ is easily reduced to H$_2$ in an H$_2$ saturated solution, and H$_2$ becoming oxidized to H$^+$ in a strongly acid solution against the equilibrium principle. How can the H$_2$ gas is involved from a basic solution where there is practically no H$^+$ ions? Another equilibrium has been postulated, H$_2$ (soln) = 2H (adsorbed on metal) = $2 H^+ + 2e$. This paper reports the results of studying the H$_2$ electrode using various techniques, such as adsorption, bubbling with H$_2$, and N$_2$, charging, discharging, and recharging, replacing the salt bridge with a conducting wire, etc. An interesting overpotential was observed that bubbling H$_2$ into the solution caused a sudden change of potential to more negative without changing the solution pH. The H$_2$ may be replaced by N$_2$ to give a similar calibration curve without the overpotential. The results contradict the redox mechanism. When the Pt is separated by H$_2$ coating, it cannot act as a catalyst in the solution. Our results seem to explain the H$_2$ electrode mechanism as the combination of its overpotential and capacitance potential. Bubbling of H$_2$ or N$_2$ only removes interfering gases such as O$_2$ and CO$_2$. Since neither H$_2$ nor N$_2$ is involved in the potential development, it is improper to call the H$_2$ or N$_2$ electrode. A term of pH / OH Pt electrode, like the pH / OH glass electrode, is suggested.

**Keywords:** capacitor, overpotential, redox, interface, adsorption, N$_2$.

1. Introduction

The reaction of the H_2 electrode has been commonly reported as $H_2 == 2 H^+ + 2e$. Since the H^+ and H_2 are in the solution and the Pt electrode does not take part in the overall reaction, the H_2 electrode is considered to be a redox electrode. Two different reaction mechanisms are discussed which may be the Volmer-Tafel mechanism [1, 2].

$$H^+ \ + \ e \ == \ H \qquad\qquad \text{(Volmer reaction)}$$

$$H \ + \ H \ == \ H_2 \qquad\qquad \text{(Tafel reaction)}$$
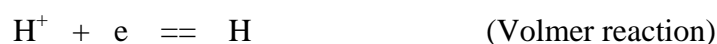
Under certain condition, particularly in an alkaline solution, the Volmer reaction must be modified to be

$$H_2O + e \ == \ H + OH^-$$
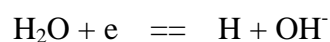
The second reaction mechanism of importance for the H_2 electrode is called the Volmer-Heyrovsky mechanism. The complete reaction is

$$H^+ + e \ == \ H \qquad\qquad \text{(Volmer reaction)}$$

$$H^+ \ + H \ + e \ == \ H_2 \qquad\qquad \text{(Heyrovsky reaction)}$$

The Heyrovsky reaction as well as the Volmer reaction can proceed with H_2O molecules. This will be the case particularly in alkaline solution. The whole reaction is

$$H_2O + H + e \ == H_2 + OH^-$$
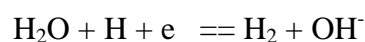
The redox reaction is represented by the Nernst equation.

$$E = E^o \ + \ RT/2F \ln ([H^+]^2 / P_{H2})$$

There is an important difference between the H_2 electrode and other reversible redox electrodes. It is that the exchange equilibrium

$$H_2 (soln) == \ 2 H^+ (soln) \ + \ 2e \qquad\qquad\qquad (1)$$

is not established in the solution phase [1] . If an inert metal electrode is placed in a solution containing H_2 and H^+, it will assume a potential defined by this equilibrium for the equilibrium does not exist [2]. It must assume to have a catalytic reaction. The above is a brief review and found in analytical chemistry textbooks. We do not report theoretical and kinetic papers on H_2 electrode here because they did not provide any experimental evidence for the mechanism. Before we are sure to know the catalytic reactions, it is a black box covered with a "catalysis" sign. It is not convinced for

the following reasons:

    a. Evolution of H_2 at a cathode is opposed.

    b. It should be a requirement that the second step of the electrochemical description of hydrogen atoms occur in one cooperative act.

    c. No H^+ production from H_2 has been confirmed.

    d. The theoreticians made the redox assumption at the beginning to calculate the kinetics before ascertaining the mechanism [2]. Reaction mechanisms must be confirmed experimentally. In summary, the earlier work was deficient experimentally. Any theory of how the H_2 electrode works must be judged by its usefulness and experimental evidence.

2. Results and Discussion

2.1 Use of Pt Wire Instead of Salt Bridge

Our results contradict the existing redox mechanisms. If the H_2 electrode acts as a redox cell, there must be a salt bridge to balance the ionic concentrations in the two compartments. Now if we could measure the Pt black potential with a Pt wire, Fig. 1, it would mean we measured the potential requiring no ionic balance. This also means that we measured capacitance potentials [9]. Any redox reactions consisting of two half-cells need a salt bridge. The calibration curves, one with a Pt wire and one with a salt bridge, are shown in Fig. 2. They are identical. The salt bridge can also act as a conducting wire.
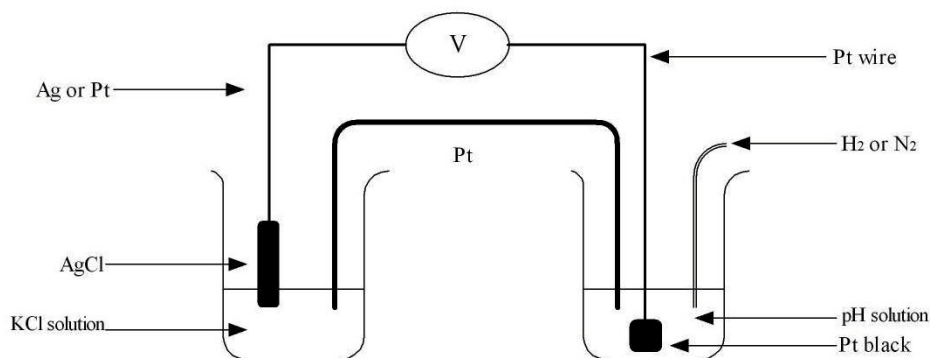

Figure 1. Experimental setup. Ag/AgCl or Pt/AgCl electrode is dipped progressively in a solution of KCl. Potentials are measured against a constant pH glass electrode.

2.2 Nernst Hiatuses

The Nernst equation has been commonly used to explain the H_2 electrode potential, because it has been assumed that there are equilibrium redox reactions involved in the H_2 electrode potential development. This assumption is questionable because we have not found any experimental evidence of redox reactions for the H_2 electrode. In the literature, it has generally explained all electrode

potentials with the Nernst equation, neglecting the capacitance potential. In recent years, the first Nernst hiatus [5] and the second Nernst hiatus [6] have been reported as it has been misused. It can only be applied to the reversible redox reactions, not to the overpotential or the capacitance potential. In discussing the H_2 electrode mechanism, the equation (1) is commonly cited, $E = E^o + 0.059 \log$ ($[H^+]^2 / P_{H2}$). This equation shows no relationship of potential and $[OH^-]$, and indicates that the potential should be inversely proportional to the H_2 pressure. On the contrary, it was found that the Pt black electrode potential was directly proportional to the H_2 pressure [3, 4]. Furthermore, after stopping bubbling H_2 we did not notice any H_2 gas generated on the Pt electrode surface.
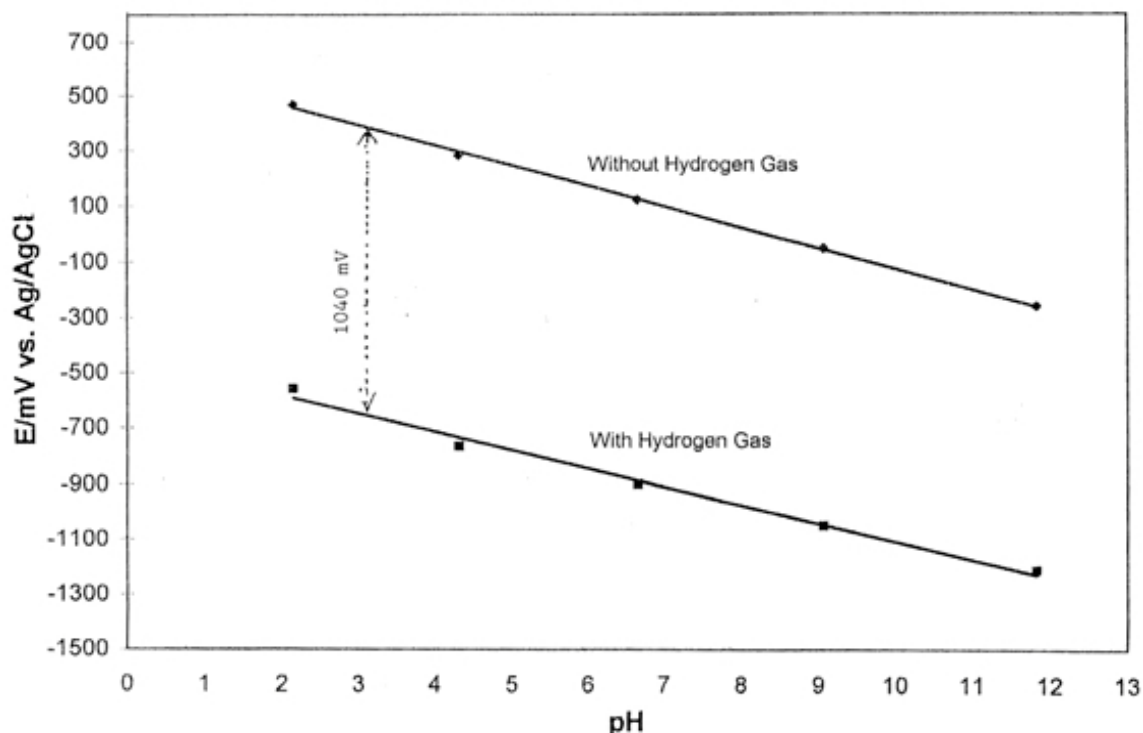
Figure 2. Calibration Curve with Pt-Black as Indicator Electrode Overpotential Effect.

2.3. Charging, Discharging and Recharging in Connection with Overpotential

Charging, discharging, and recharging have demonstrated that the Pt electrode potential could be developed to a more negative potential (Figs. 3-5). This shows the case of polarization, overpotential (η = Ei − Ee.). This polarization was formed due to the adsorption of a layer of H_2 at the Pt electrode interface. The non-conducting gas inhibits the electron current flow. The H_2 overpotential was found to be approximately 1040 mV. The misapplication of the Nernst equation to the overpotential is an example of the first Nernst hiatus as pointed out by Bockris [5]. The results shown in Figs. 3-5 indicate the storage of charges at the Pt electrode surface; this is the case of a capacitor, not the redox reactions in the solution. Because we could measure the capacitance potential with a conductor instead of a salt bridge, there was no need of balancing ionic concentrations with a limited current. On the other hand, for redox reactions, the electron transfers are taken place in the solution or at the electrode surface. Now the Pt surface is blocked by the H_2 gas. Adsorption of H^+ and OH^- ions at the inner and double layers has caused the Pt electrode potential changes. In the presence of a thin layer of H_2 at the Pt interface, the H^+ and OH^- ions still could diffuse to the Pt surface slowly (Figs. 3-6). In an acid

solution, the potential is relatively positive, in a basic solution the potential is much more negative .We could not determine the amount of H^+ and OH^- ions adsorbed on the Pt surface assuming that they were at the interface inner or double layer. But we noticed that addition of acid to the Pt black suspension caused its rapid coagulation, meaning a neutralization of negatively charged Pt colloidal particles by the positively charged H^+. With addition of a NaOH solution to the suspension, no coagulation was observed .In the near neutral solutions, we observed adsorption of H^+ and OH^- by the Pt black particles. If more Pt black was added (say, 5 g. instead of 0.5 g), more pronounced H^+ and OH^- adsorptions would be observed (Table 1).

**Table 1.** Adsorption of H^+ and OH^- by Pt black powder in different pH solutions.

	pH of solution						
Before adding Pt black	1.24	2.21	4.31	6.50	9.43	11.79	1.44*
After adding Pt Black	1.26	2.22	5.26	6.25	7.15	11.60	1.44

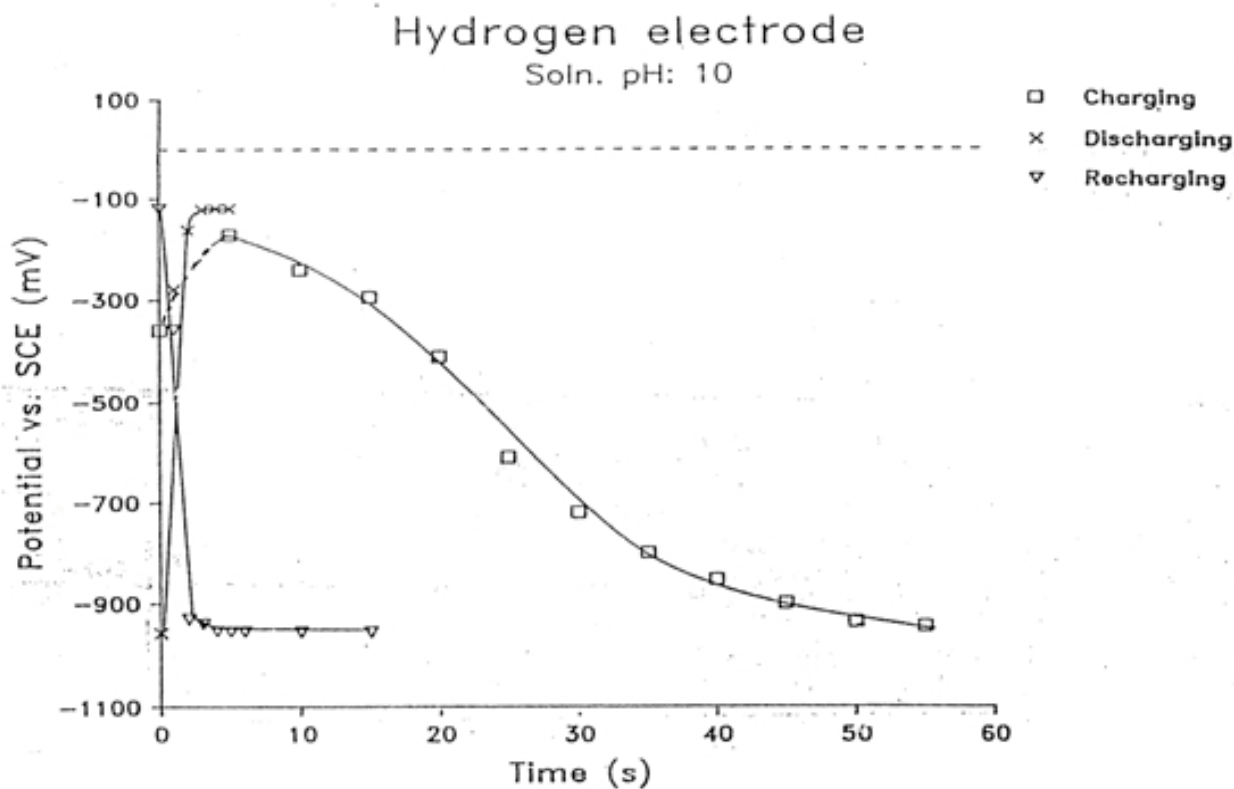5.0 g of Pt black powder was added to 20 mL of un-buffered solution. Bubbled with H_2 gas.

* No H_2 gas added.
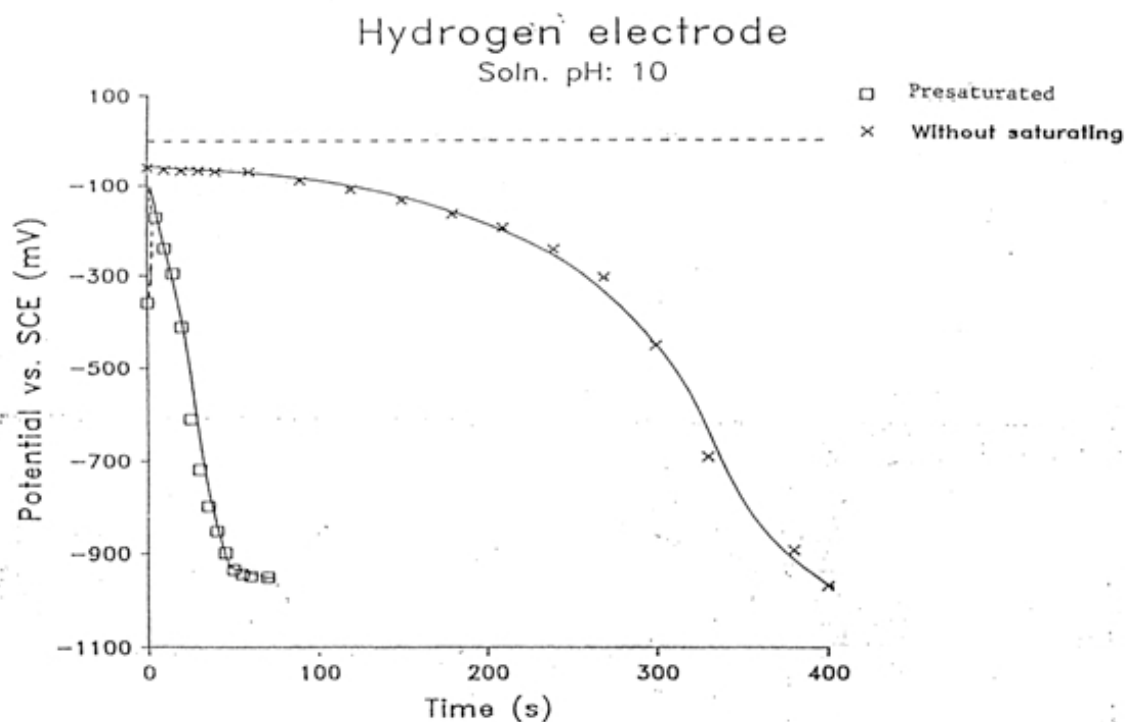
Figure 3. Potential changes during charging of hydrogen electrode both with and without presaturation of solution with H_2 gas.
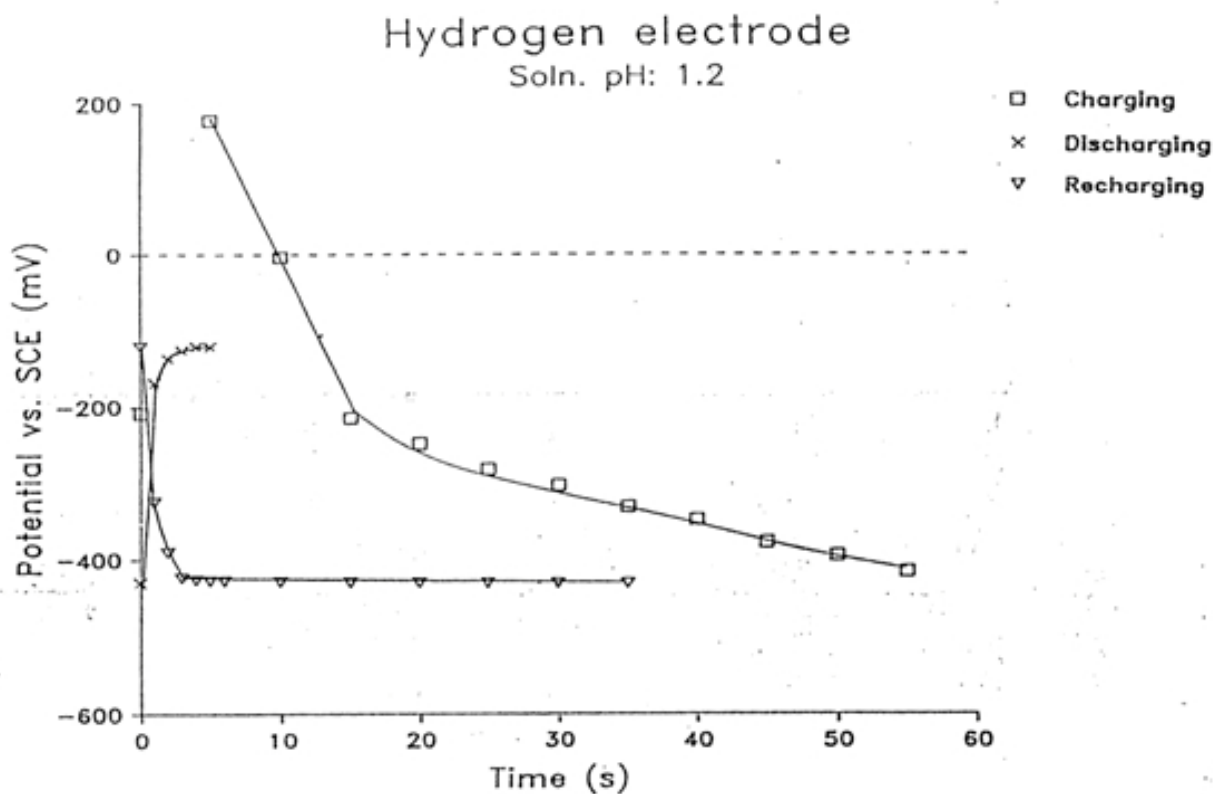
Figure 4. Potential changes during charge, discharge, and recharge of
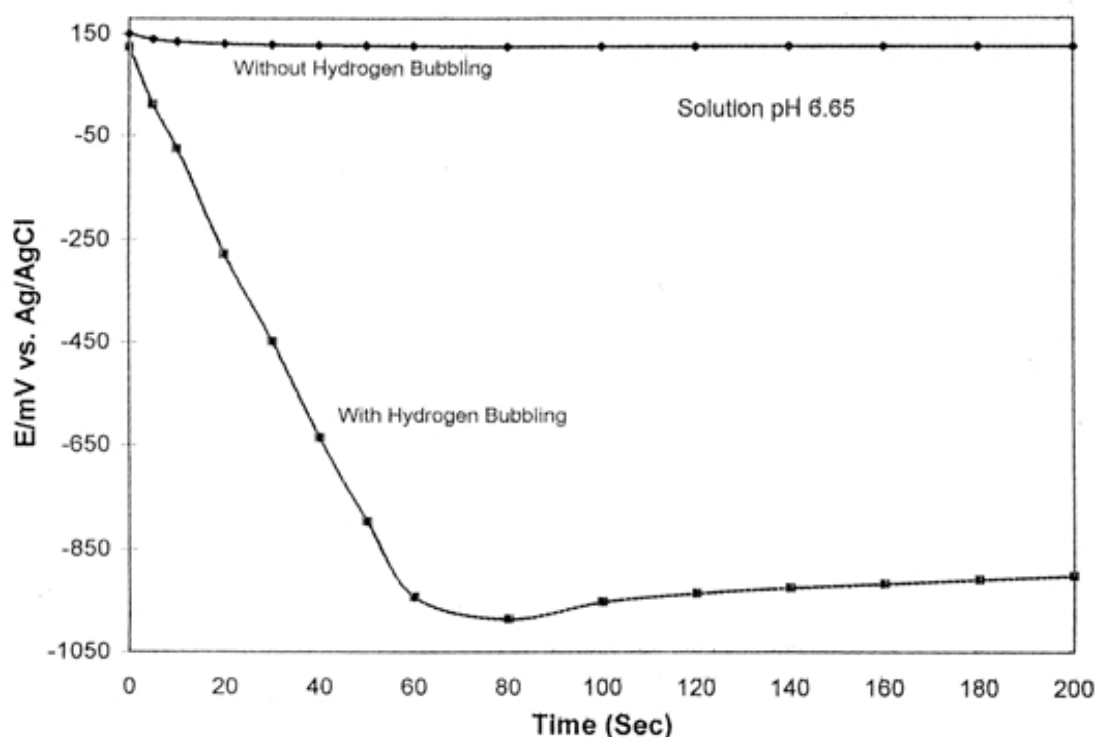hydrogen electrode (solution pH: 1.2).

Figure 5. Potential changes during charge, discharge, and recharge of
hydrogen electrode (solution pH: 10).

2.4. Stirring Effect

Experiments with stirring effects were carried out with a stirring bar without bubbling H_2 or N_2. Stirring made the potential move to more positive, after stopping the stirring, the potential returned to the original potential [8] (Figs. 7-8). This indicates that stirring did not cause any redox actions, it only disturbed the double layer or triple layer [11]. It is possible that some of N_2 was also adsorbed on the Pt, when stirring took place, spinning off the N_2, the overpotential effect decreased. However, Hills and Ives stated that in both acid and basic solutions caused polarization [1]. Such different results may need further studies. At least the polarization by stirring is recognized. Also, stirring changes the electrode potential by removing the counterion triple layer and part of double layer [11].

2.5. *pH of the Solution Was Independent of Pt Black Electrode Potential*

The overpotential of H_2 electrode potential was discussed [1]. The results in Fig. 9 show very interesting overpotential phenomena that the electrode changed to very negative potentials with bubbling H_2, meantime the solution pH was kept constant. This means that the solution pH was independent of the electrode potential, it does not agree with the Nernst equation. This is another misleading use of the Nernst equation. If we subtract the constant overpotential, we could obtain the smooth calibration curves (Fig. 2). After stopping bubbling H_2, we introduced the N_2, the potentials gradually returned to more positive at the original position. It seemed that the H_2 overpotential effect could be removed by N_2 because the Pt adsorbs only insignificant amount of N_2 (Figs. 10, 11). These potential changes were mainly caused by physical actions, not by the redox or chemical electron transfers in the solution. We want to stress that our statements are based on our experimental results, not speculative reactions with many mathematical equations.

Figure 6. Change of Pt – Black Electrode Potential with or without Hydrogen Gas.
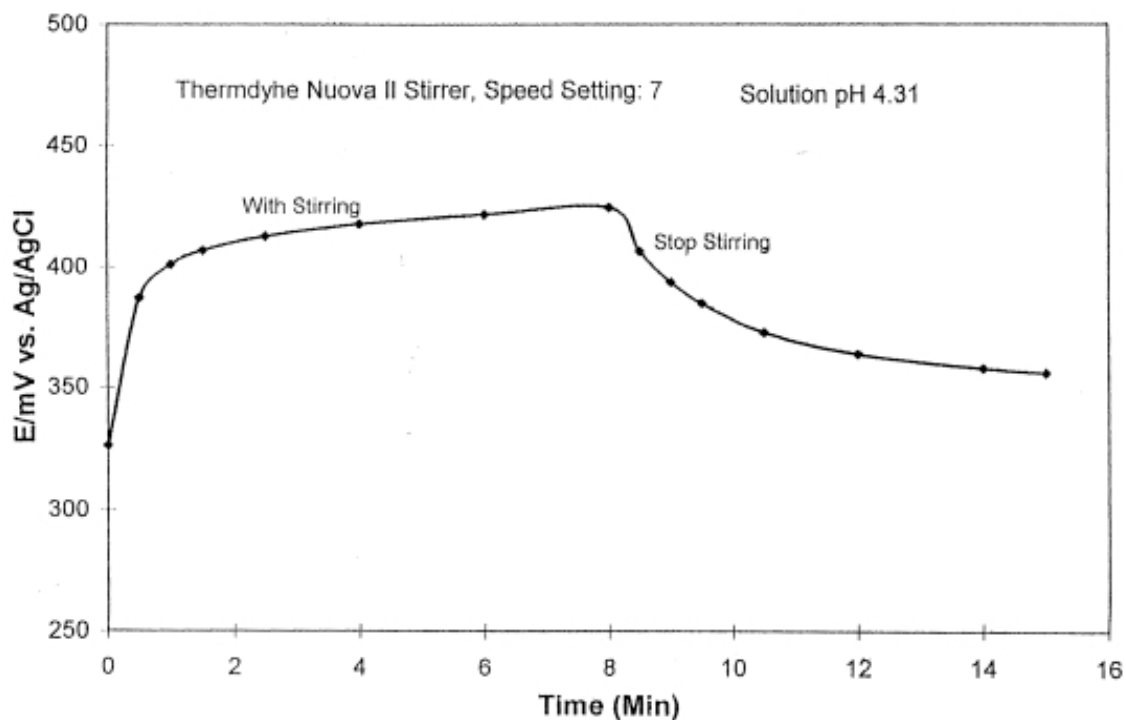
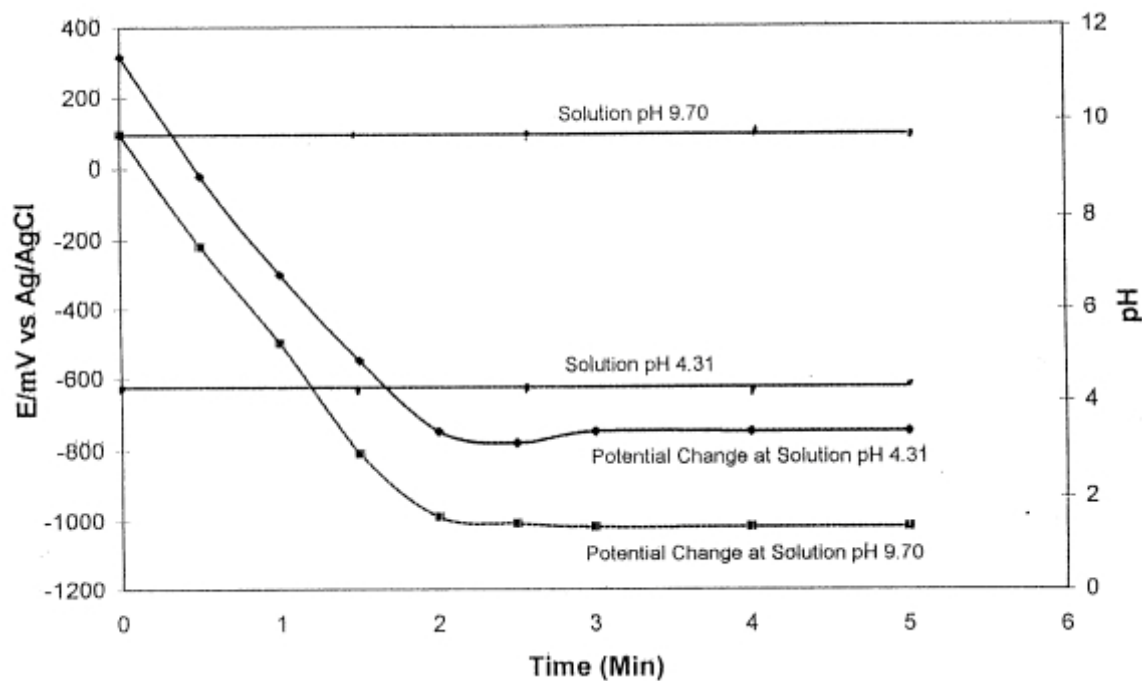**Figure 7.** Stirring Effect on Potential of Pt – Black Electrode in Acidic Solution.
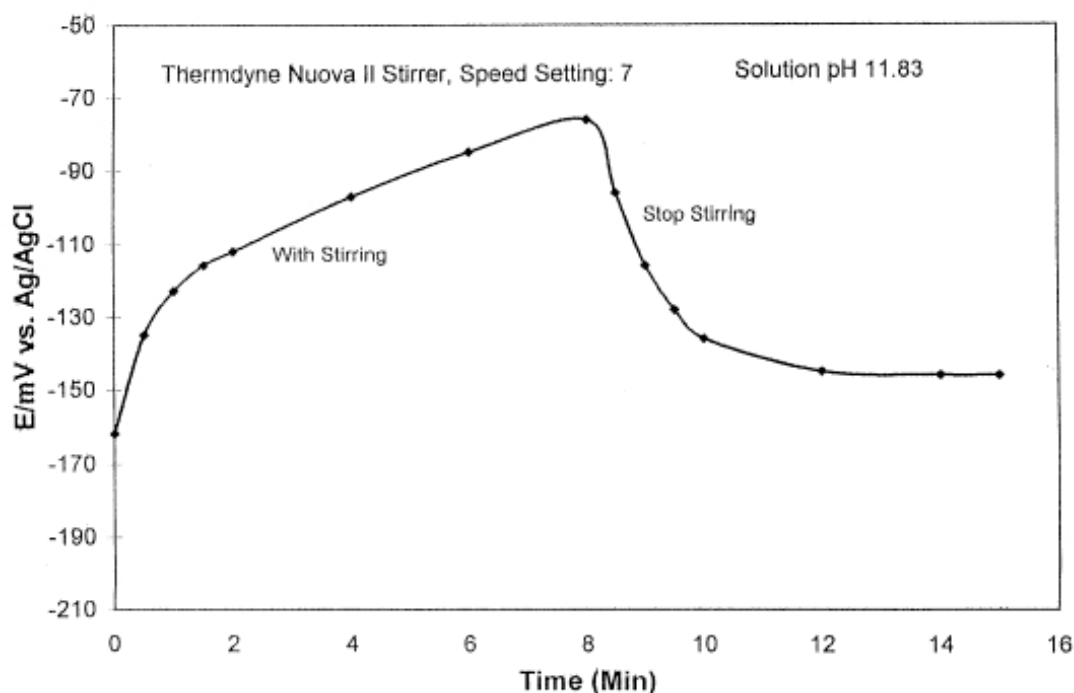
Figure 8. Stirring Effect on Potential of Pt – Black Electrode in Basic Solution.

2.6. No Catalyst

No apparent catalytic reactions were observed. We need experimental evidence to show any catalytic actions of Pt black electrode. We have not found any evolution of H_2, or formation of H^+ from H_2 gas.

In the literature, it was assumed that the electron comes from Pt. This seems unlikely because if it comes from Pt, the electrode potential should be positive instead of becoming very negative with bubbling H_2. When Pt is separated from the solution by the H_2 adsorption, it cannot act as a catalyst in the solution. The proton reduction needs applying a certain voltage, without applied potential there is no H_2 gas evolution [13]. In the H_2 electrode no potential is applied, its potential is measured.

Figure 9. Effect of Bubbling Hydrogen Gas on Potential of Pt – Black Electrode in Acid and Basic Solution.
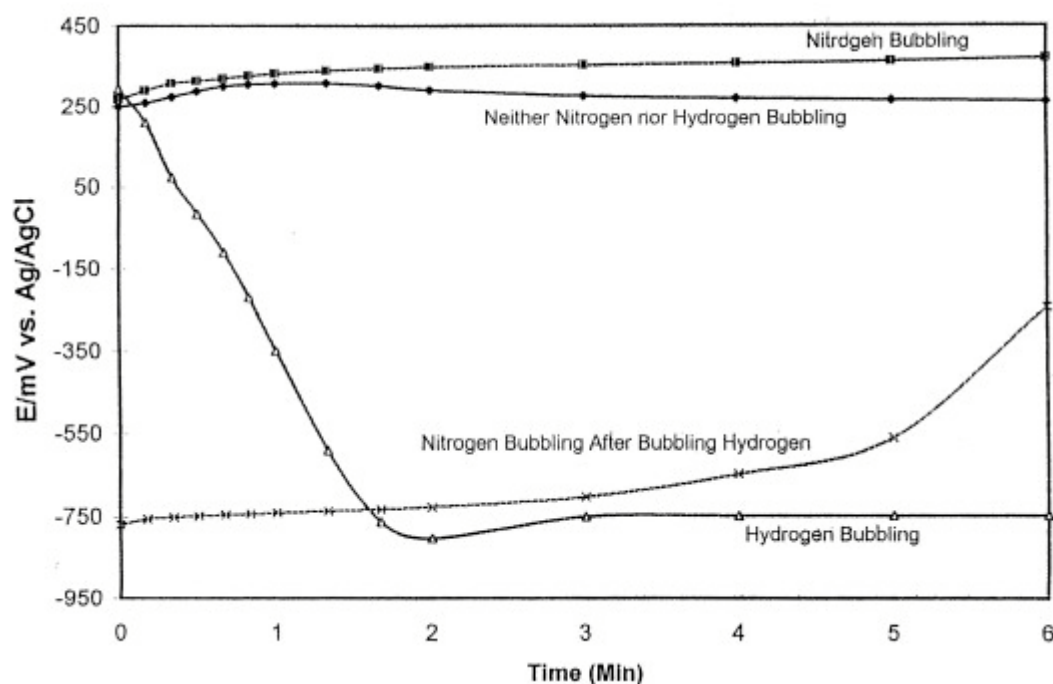
Figure 10. Effect of Bubbling Hydrogen or Nitrogen Gas on Potential of Pt – Black Electrode at pH 4.38.
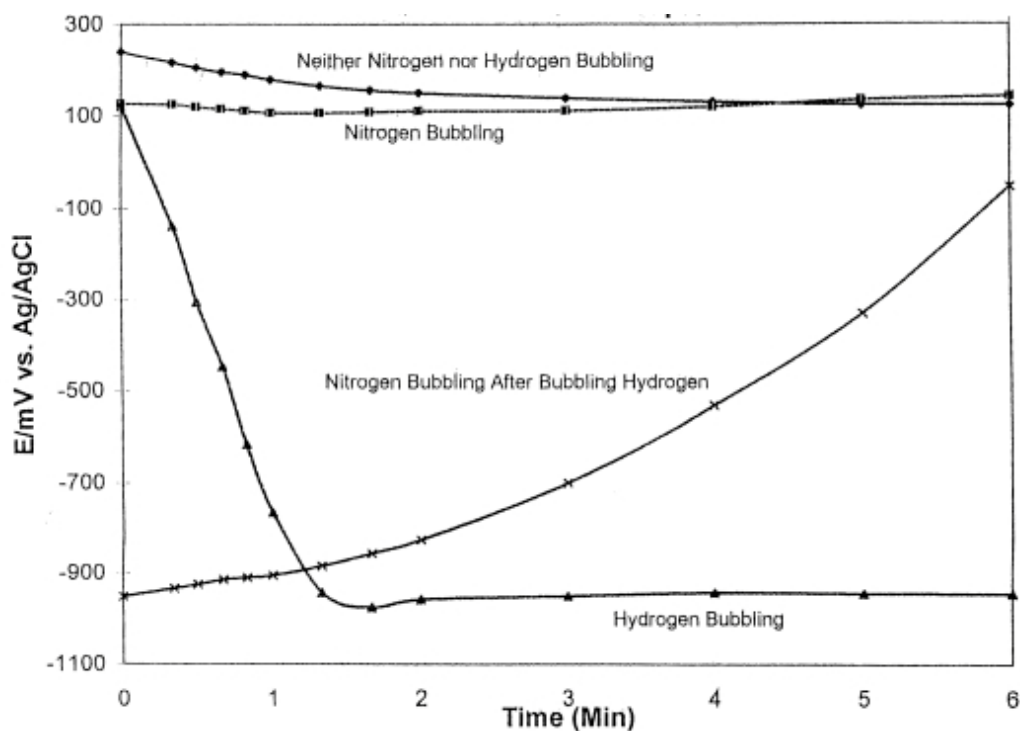
Figure 11. Effect of Bubbling Hydrogen or Nitrogen on Potential of Pt – Black Electrode at pH 8.50.

2.7. Interference

It is known that H_2 may react with O_2 in the presence of Pt as a catalyst. In the case of the Pt black electrode, the O_2 is removed by bubbling with H_2 or N_2. Other substances interfere as they tend to be adsorbed on the surface to occupy the active sites. Potassium phthalate and $FeSO_4$ are known to interfere. Assume that many other substances would interfere, as the H_2 electrode is not a selective technique for pH measurement and used as a reference electrode in a separate container [1].

3. Experimental Section

The Pt black was prepared from the $PtCl_6$ by electroplating it on a Pt strip [1]. The reference electrode was the Ag/AgCl or SCE in a separate beaker containing 3.5 M KCl instead of a commonly used salt bridge, a Pt wire was used (Fig. 1). The pH of the solution was determined by the Weiss Research pH glass electrode and a separate pH meter.

4. Conclusions

Our results have contradicted the prevailing redox mechanisms of the H_2 electrode. We believe that it is not a half-cell but instead a capacitor. Its potential is a combination of its overpotential and capacitance potential. The Nernst equation applied to the H_2 electrode potential mechanisms, conventionally described in the textbooks, needs to be critically reviewed and scrutinized. We have obtained a calibration curve for potential vs. pH using a Pt wire without a salt bridge and H_2 bubbling which are required in the redox reactions. The H_2 may serve the purpose of removing the O_2, and other

interfering gases. Since H_2 tends to be adsorbed at the Pt interface interacting with the double or triple layer, the overpotential is resulted in a tremendous negative potential drop. The potential changes are mainly originated from physical actions, not redox reactions. The Nernst equation cannot explain the potential in the alkaline solution because the OH^- does not participate in the redox reactions. And there is practically no H^+ ion in a basic solution. Stirring also caused the Pt electrode potential changes, not as great as the potential change caused by bubbling with H_2, 1040 mV, but meantime the solution pH had remained constant. When Pt is separated from the solution by H_2, there is then little chance for Pt to catalyze any redox reactions in solution. This has clearly demonstrated that the Nernst equation has nothing to do with the Pt black. Redox electrodes are not suitable for acting as a reference electrode because they are easily subject to interference. Hills and Ives emphasized that "No simple conclusions emerge upon which to build a general theory of the H_2 electrode" [1, p. 83]. Reaction mechanisms must be found by experiments, not by speculation, imagination, or illusion. We should realize that for the H_2 electrode the plane Pt does not work, it needs the Pt black with a large amount of surface area for ion adsorption as a capacitor. We have found the adsorption property of Pt black electrode to offer an unusually high sensitivity. The calibration curve slope reached to be 260 mV/pH at pH 3-5, instead of regular 59 mV/pH, with a capillary function [14]. This is another proof of the evidence of adsorption mechanism. In addition, the charging, discharging, and recharging results clearly demonstrate the origin of electrode potentials.

We would like someone to repeat our experiments and offer their interpretations. Our results may be just the beginning to stimulate further studies on the double and triple layers of Pt electrode interface. We welcome any new ideas and mechanism with experimental supports. Recently the IUPAC Analytical Chemistry and Physical Chemistry Divisions solicited suggestions on pH definition and mechanism concept [12]. Readers may find our unconventional results interesting and try some fresh ideas. In practice, our results will not change anything for the H_2 electrode, we still take it as a standard reference electrode, arbitrarily to be $E^o = 0.00$ V. We may change its mechanism, E_{red} to $E_{capacitance}$. We would like to emphasize that in order to understand how the electrode works we must find its mechanism experimentally with correct assumptions. Any theoretical speculations must be verified by facts and logics. It is important to teach our future chemists the correct concepts and mechanisms of the fundamental reference electrode. We like to emphasize that all commonly used important reference electrodes, H_2 , calomel, Ag/AgCl, and pH glass electrodes are capacitors, not redox half-cells.

Acknowledgments

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