

THE PREPARATION OF HYDROGEN
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The electromotive force established at the junction of a gaseous or a metallic conductor and an electrolytic conductor represents essentially the work involved in the taking on of electrons at the cathode and the giving up of electrons at the anode. Theoretically, in the case of gas electrodes, this potential difference should be independent of the metallic conductor used for making electrical contact with the gas, provided it does not react chemically with the latter or the solution in which it is in part immersed. It also follows that if the electrode, for example, hydrogen, is a reversible one, its potential when acting as a cathode in an electrolytic cell or an anode in voltatic cell should be the same. In practice, however, it is found that because of irreversible effects of one form or another, these conditions are not realized. The problem therefore of determining the methods for the preparation of gas electrodes that most nearly approximate a reversible system becomes an important one. This is especially true in the case of the hydrogen electrode in view of the very extensive applications that have been made of the electromotive forces associated with the H_2 , H junction or the $\text{H}_2 \rightleftharpoons 2\text{H} + 2(-)$ electrode reaction.

The early work of Le Blanc¹ first established the hydrogen electrode as a reversible system. Smale² and Wilsmore³ in their subsequent researches came to the same conclusion. Following these early investigators there are a considerable number of others who have studied it with special reference to its constancy and reproducibility. Among these may be mentioned in particular Loomis and Acree⁴, Lewis⁵, Ellis⁶, and Clark⁷. Other workers have confined themselves more particularly to the applications of the hydrogen electrode. In spite

¹Le Blanc, Z. Physik. Chem. 12, p. 333 (1893).

²Smale, Z. Physik. Chem. 14, p. 520 (1900).

³Wilsmore, Z. Physik. Chem. 35, p. 296 (1900).

⁴Loomis and Acree, J. Physic. Chem. 19, p. 660; J. Am. Chem. Soc. 46, p. 621; J. Am. Chem. Soc. 46, p. 585.

⁵Lewis, Brighton, and Sebastian, J. Am. Chem. Soc. 39, p. 2245.

⁶Ellis, J. Am. Chem. Soc. 38, p. 742.

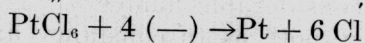
⁷Clark, W. M. Determination of $\text{H} + \text{I}$ on concentration. 2nd Ed. 1922.

of all the work carried out in the past there has still been much uncertainty as to the best procedure to follow in the preparation of the electrodes, particularly with regard to the current densities and composition of solutions which are most suitable. The situation in this respect is summed up very well by Clark in the second edition of his book on "The Determination of Hydrogen Ions". On page 177 the following statement appears: "No detailed descriptions have been found in the literature and those that are found are quite inadequate to account for the varied deposits sometimes formed." The present paper represents an attempt to supply some of this information.

The three materials most commonly used in the preparation of hydrogen electrodes are electrolytically deposited platinum, palladium, and irridium. The latter is recommended by Lewis, Brighton and Sebastian⁵. Two objections to the use of irridium are the high cost of the metal and the extreme difficulty of getting it into solution. In the case of palladium it is easy to obtain electrolytic deposits but it was our experience that these deposits did not adhere well, especially when the electrodes were used in acid solution. As regards the procedures previously described in the literature for the preparation of the platinized platinum electrodes, comparatively few of these make use of solutions of the pure chloroplatinic acid. Whenever this is done the metal is usually described as being deposited by means of a commutated current with a sufficiently high current density to cause a copious evolution of gas at each electrode. Some writers call attention to the difficulty of depositing platinum from solutions of chloroplatinic acid alone. This is illustrated in the following statement as made by Fox⁸: "It is not possible to get a good deposit of platinum black on a very pure specimen of platinum foil, if the platinum chloride solution employed is also very pure. A trace of lead acetate is usually added to the solution, therefore, and it is necessary to remove every trace of this from the electrode after coating, or good values are unobtainable." The experience of the writers was similar to that of Fox both with regard to the deposition of platinum directly on a platinum base and the use of lead acetate.

⁸Fox. Chem. News. 100, p. 161.

In view of the situation as described above it was decided to investigate in a somewhat systematic way the necessary conditions for the deposition of platinum in a form suitable for hydrogen electrode purposes from solutions of pure chloroplatinic acid. In this connection attention might first be called to the electrode process involved. The reaction resulting in the deposition on the cathode of the metallic platinum is presumably that represented by the equation



The problem involved in particular a study of the concentration and the current density relations and also of the character of the metal to be used as a base. For this purpose the following plan was adopted. Solutions of chloroplatinic acid obtained from the Bureau of Standards were prepared, ranging in concentration from one to six percent by weight of acid. Electromotive forces varying in steps of 0.2 volt were impressed across the platinum foil electrodes of one sq. cm. until a deposit was formed on the cathode. Following this the effect of increasing the current density was noted. It was found that good, black, velvety deposits could be obtained, provided the current density was kept low and the concentration sufficiently dilute. As regards the current density, the results were best when the electromotive force was so adjusted as to just prevent the evolution of hydrogen at the cathode. When higher current densities were used the metal did not adhere properly. The concentration found to be most satisfactory was a 1-2 percent solution. With an increase in concentration the deposit became gray and crystalline; when the six percent solution was used it was distinctly crystalline in appearance—a form altogether unsuited for hydrogen electrode purposes. On account of the low current density the time required is necessarily longer than would otherwise be the case. It was found that a uni-directional current passing for from three to four hours would give a uniform black deposit that adhered very well to the electrode.

The condition of the surface of the electrode is obviously a very important factor in getting good deposits. In this connection we found that it was much easier to

bring about a satisfactory deposit of platinum if the electrode was first gold plated. In the case of old electrodes the gold plating appears to be almost a necessary prerequisite. One advantage of electrodes prepared with a gold base is that they seem to require less time for saturation with hydrogen gas. Also, the process of cleaning the electrodes is much simpler than if the deposit is made directly on a platinum base.

Electrodes prepared in this manner described above were tested in considerable numbers. The results were very satisfactory both as to constancy and the electromotive force values for electrochemical systems. The electrodes have also been used by students in electrochemistry courses with better results than previously obtained by other methods.