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Modified Static Mercury Drop Electrode

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Several problems such as metallic contamination due to amalgamation, capillary plugging and air leaks are associated with the use of the static hanging mercury drop electrode (SHMDE). This paper describes the design and construction of an improved version of this type of electrode. The modifications include an improved valve seat and capillary attaching assembly.

INDEX DESCRIPTORS: Polarography, Capillary, Construction

Polarography is a special form of voltammetry which employs a dropping mercury electrode as its working electrode. Mercury has enjoyed a special place in voltammetry because of its high overvoltage with respect to hydrogen deposition and the ease with which a clean reproducible electrode surface is obtained. The most common method of forming the electrode has been to utilize the droplet produced as the mercury, pulled by the force of gravity, issues forth from a capillary tube. Such an electrode is referred to as a dropping mercury electrode (DME). The rate of flow is controlled by the internal diameter, length of the capillary and height of the mercury column above the capillary orifice. The droplet falls off the capillary when the weight of the droplet exceeds the surface tension of the mercury. A new droplet begins to form immediately. For certain applications operators have found it advantageous to prematurely dislodge the drop using a mechanical tapper. Such techniques make it easier to more precisely control the drop time.

Despite its many advantages the dropping mercury electrode suffers from certain disadvantages that limit the applicability of the polarographic technique. Polarography is based upon the measurement and interpretation of current-voltage curves that are obtained when a voltage is applied to the dropping mercury electrode. The total measured current flowing across the solution-electrode interface in an electrochemical cell is composed of two components, the faradaic current and the nonfaradaic current. The faradaic current originates from the oxidation and reduction processes that occur at the interface and result in the flow of electrons within the electrode. Other processes occurring at the interface may result in a current flow without the concomitant redox reaction. Such currents are, therefore, called nonfaradaic. The analytical usefulness of the polarographic technique requires the measurement of the faradaic current rather than the total current. Thus, much research has been directed toward minimizing or eliminating nonfaradaic current. One of the principal forms of nonfaradaic current is the capacitance or charging current. As the mercury drop grows to its maximum size the surface area of the electrode likewise increases over the life of the drop, changing as a one-sixth order parabola with time. The change in the surface area necessitates change in the charge on the surface in order to maintain a constant voltage at the surface. This change in charge appears as the charging or capacitance current. At analyte concentrations of 10^{-5} molar and above the charging current is small with respect to the faradaic current and does not have a significant effect on the measurement. However, at concentrations below that level the magnitude of the faradaic current is decreased to the extent that it is of the same order of magnitude as the nonfaradaic current. Consequently, a practical analytical scheme requires the elimination or separation of the two currents.

Princeton Applied Research Corporation (PAR) has developed a new type of dropping mercury electrode, the static hanging mercury drop electrode (SHMDE). The PAR Model 303 static mercury drop

electrode represents a radical departure from the conventional dropping mercury electrode. In this new device a wide bore capillary is used together with a short column of mercury. The top of the capillary column itself serves as a valve seat for a solenoid-activated plunger type valve which is used to stop the flow of mercury. Electrical contact between the mercury on both sides of the closed valve is maintained by coating the top portion of the capillary with fused tin oxide as an electrical conductor. The mercury used in this device comes into contact with plastic, stainless steel, and a spring wire within the electrode.¹ These contacts may result in contamination of the mercury. Although said contaminants may be at low levels of concentration they can become a major hindrance in the determination of trace and ultra trace metals.

In order to minimize mercury contamination resulting from unnecessary metallic contact, Buchanan and Soleta² built a plastic adaptation of the SHMDE so that only the metal used as the electrical contact actually touched the mercury. In addition, a lower electrode resistance was achieved by making the valve seat a part of the reservoir and establishing the electrical connection below the seat, in a narrow channel just above the capillary. As a result of these modifications the fused tin oxide tipped capillary was no longer required.

Sturrock and Williams³ also found that it was desirable to reduce the electrode resistance by incorporating a valve seat within the reservoir itself rather than utilizing the top of the capillary column. Their modification retained the use of stainless steel and thus electrical contact with the effluent mercury could be maintained through the stainless steel case. Their work did not point to a solution of the problem of providing an effective air seal between the reservoir and the capillary. In the Buchanan and Soleta modification it was very difficult to obtain a good seal between the capillary and the surrounding case. Air leakage at this point made the drop formation unreliable therefore, considerable effort was necessary to ensure an appropriate seal.

This paper describes a further modification of the Buchanan and Soleta version of the electrode, including the incorporation of an improved spring tension adjustment scheme as well as the adaptation of the capillary seal as recommended by the Sturrock and Williams model. Figure 1 shows an overall view of the electrode assembly. The material of construction chosen was 6.35 mm Plexiglas plastic sheets and cast round stock. Preference for the cast round stock rather than the extruded round accrued because the extruded material tended to crack and split if stressed or placed in contact with solvents which could release internal strains. The source of the sheet material did not matter. With the exception of the capillary seal components the overall dimensions of the electrode are not critical. The mercury reservoir had the shape of a box measuring 57.15 × 63.50 × 63.50 mm in size. It was constructed of 6.35 mm plexiglass sheets.

The 31.75 mm dowel beneath the reservoir was built in two pieces, one being a plunger guide and the other serving the dual role as a valve seat and capillary attaching assembly. The plunger guide was 17.78 mm in length bored to within 3.18 mm of its length with a 12.70 mm diameter hole. The bottom of the plunger guide was bored to a diameter 4.76 mm which served to guide the valve plunger. In a circle surrounding the central hole, several smaller holes were drilled

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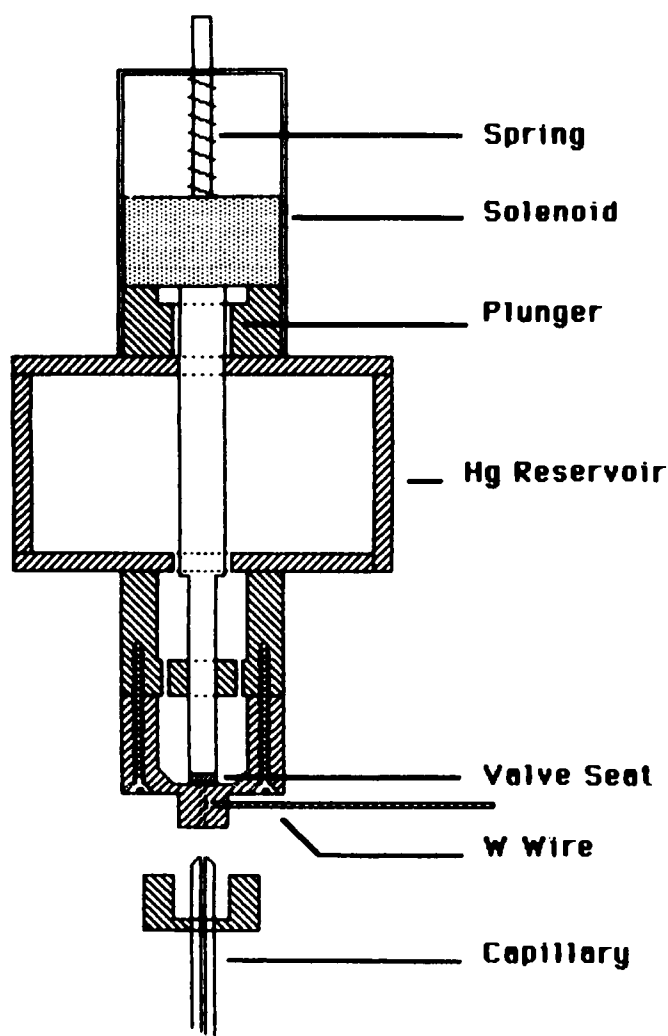


Fig. 1. Overall view of electrode assembly

through the bottom of the plunger guide to ensure the flow of mercury past the guide.

An enlarged view of the valve seat and capillary attaching assembly are shown in Figure 2. This portion of the electrode was fabricated as a single piece from 31.75 mm cast dowel plexiglass rod. A 12.70 mm diameter hole was bored to a depth of 12.70 mm and then tapered 9.40 mm over a further depth of 3.18 mm. The bottom of the bore was machined flat and smooth. It serves as the valve seat. From the opposite end a 9.53 mm diameter hole was bored to a depth of 7.14 mm. The bottom-center of the bore was then tapered with a mill of the same taper as the top of the capillary to a depth slightly less than the tapered top of the capillary thus ensuring a good fit. A hole was drilled with a #69 drill to connect the two borings and provide a path for the mercury between the valve seat and the glass capillary. A second hole was drilled with a #60 drill into the connecting drill hole from the side to allow the insertion of the connecting electrical wire. The external diameter of the piece was reduced to a value of 12.70 mm over a length of 15.88 mm from the bottom. This length was then threaded and a corresponding cap nut was prepared which would be used to attach the capillary to the valve assembly.

A ferrule was attached to the glass capillary 6.35 mm from the end of the capillary. A plexiglass collar 14.25 mm long and 7.94 mm in

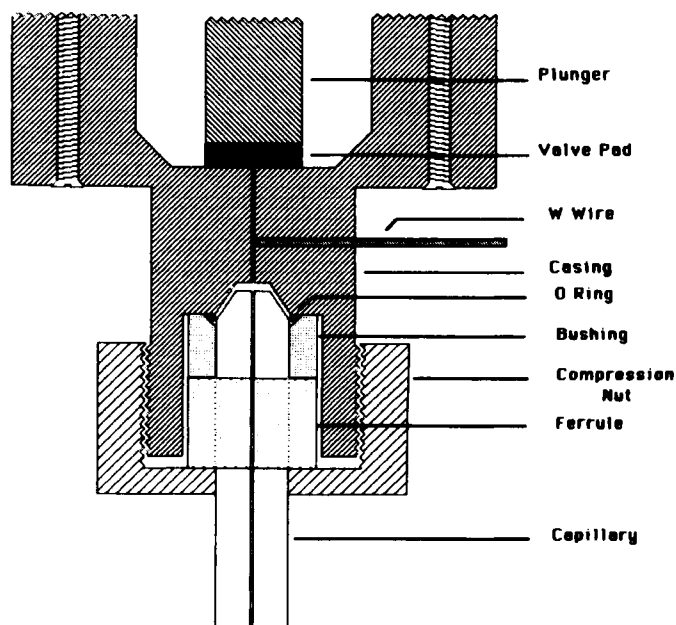


Fig. 2. Enlarged view of valve seat and capillary attachment assembly

diameter was drilled and reamed to 3.97 mm (capillary diameter). The top end of the collar was tapered towards the center so as to provide good compression of the "O" ring seal between the capillary and the assembly when held in place by the cap nut on the bottom.

Upon completion of the electrode assembly a test of the reproducibility of the drop size and hence its surface area was undertaken. For this test the electrode was attached to the square-wave polarograph described in reference 3. A potential of -0.5 volts was applied to the electrode and without changing the applied potential a sequence of eleven (11) drops of mercury were formed and dislodged. These droplets coalesced to a single droplet which was collected, washed with distilled water and dried with acetone. The dried droplet was transferred to a small watch glass and weighed. The mass of an individual drop was taken as one eleventh that of the coalesced droplet. The drop was assumed to be spherical; so given the density of mercury it was possible to calculate the volume of the drop and therefore the radius of the drop. From the radius the surface area of the drop was then calculated. This entire procedure was repeated ten times. The average surface area of the electrode was calculated to be 0.032 cm^2 with a standard deviation of 0.002 cm^2 .

The use of this electrode was successful in that the oscillations produced by charging currents, as is the case with the DME, were reduced even after large amplifications of the signal. Thus, a superior signal to noise ratio was observed. The earlier problems associated with a SHMDE such as air leaks and capillary plugging, were reduced to DME quality with the new modifications. And, the mercury contamination due to metal contact was eliminated with the introduction of an all plastic design. The use of Sturrock and Williams' valve seat design with Buchanan and Soleta's all plastic design increased drop reproducibility to within a 6% change in surface area.

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