

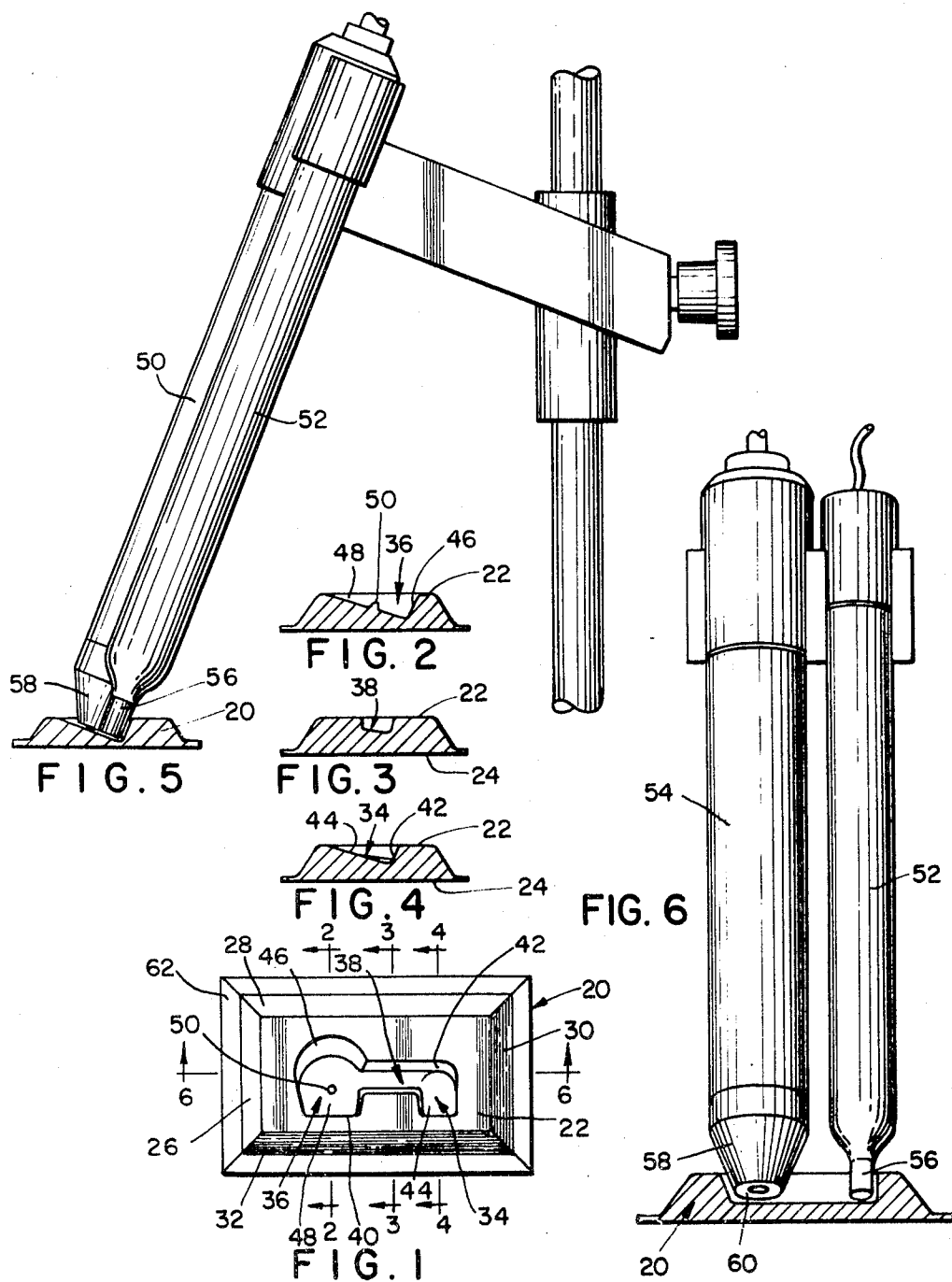
Sept. 16, 1969

M. S. FRANT

3,467,591

CONFORMAL DISH

Filed July 25, 1966



INVENTOR.
MARTIN S. FRANT
BY *Robert J. Schiller*
ATTORNEY

1

2

3,467,591

CONFORMAL DISH

Martin S. Frant, Newton, Mass., assignor to Orion Research, Inc., Cambridge, Mass., a corporation of Massachusetts

Filed July 25, 1966, Ser. No. 567,605

Int. Cl. B01k 3/00

U.S. Cl. 204—195

4 Claims

ABSTRACT OF THE DISCLOSURE

This invention concerns a dish for holding a minute sample of material for electrolytic analysis, the dish being formed to have a pair of depressions in the top surface thereto. The depressions are joined by a channel through which a fluid bridge can be formed from one depression to the other. One depression is intended to have a standard reference electrode inserted thereon, the second depression being intended to have a specific ion responsive electrode inserted thereon. Both depressions are shaped to conform to the tip configuration of the respective electrodes. The second depression also includes extending upwardly from the bottom, a small protuberance which serves to minimize the formation of interfering air bubbles at the ion sensitive surface of the specific ion responsive electrode.

This invention relates to electrochemistry and more particularly to apparatus for use in electrochemical analytical procedures involving liquid samples of limited quantity.

Electrometric determination of ionic activity in solutions using ion-sensitive electrodes is now standard technique, such as in measurement of pH. The activity or concentration of a large variety of ions can be measured by similar methods which involve the construction of a cell of the following general nature:

Electrode reversible to ion X/ solution with ion X/ Salt Bridge/ Ref. electrode.

The reference electrode is usually calomel or Ag-AgCl electrode. The reversible electrode can be of a large number of diverse electrodes well known in the art such as electrodes specific to K^+ , Na^+ , Ca^{++} , H^+ or the like. Both electrodes of the cell generally are in contact with the solution so that where the electrode configurations provide large contact surface areas, the amount of solution required is quite large also. This poses no particular problem in on-stream monitoring of ion activity in industrial processes generally where conveniently there are large quantities of solution. However, in laboratory analyses, frequently very limited sample quantities are available and it is often undesirable to increase the amount of solution by dilution because of disproportionate changes in ion activity. Also where the active sensitive area of a "dipping" type electrode is quite large and limited to a substantially flat surface, there is danger of entrapping minute air bubbles against the surface with attendant spurious results in the electrode EMF developed. For this reason, as described in detail in copending U.S. application Ser. No. 559,466, filed June 22, 1966, and assigned to the same assignee as the present application, certain electrodes preferably have at an end to be placed in contact with the sample solution, a concave or dished face surrounding the flat ion-sensitive area, all edges of the face being rounded. This tends to cause all air bubbles to coalesce and form a large central bubble which can be readily removed or washed out.

The principal object of the present invention is to provide a container or dish for use with an electrochemical analytical cell for holding limited amounts of sample solution in operative relation to a pair of electrodes. Other

objects of the present invention are to provide such a container which is shaped to closely conform to the configuration of the ends of a pair of dipping electrodes of an electrochemical analytical cell, thereby minimizing the quantity of sample solution required for a measurement of ion activity in the solution; to provide a solution sample container particularly adapted for use with a first electrode having a substantially cylindrically shaped end and a second electrode having a substantially concave cup shaped end; and to provide such a dish which is so inexpensive and simple to make and use as to permit ready discard after a single use, thereby obviating the problem of contamination from sample to sample.

Other objects of the invention will in part be obvious and will in part appear hereinafter. The invention accordingly comprises the apparatus possessing the construction, combination of elements, and arrangement of parts which are exemplified in the following detailed disclosure, and in the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is a plan view of a conformal dish incorporating the principles of the present invention;

FIG. 2 is a cross-sectional view taken along the line 2—2 of FIG. 1;

FIG. 3 is a cross-sectional view taken along the line 3—3 of FIG. 1;

FIG. 4 is a cross-sectional view taken along the line 4—4 of FIG. 1;

FIG. 5 is a side elevational view, partly in fragment, showing a pair of electrodes in operative relation to the embodiment of FIG. 1, the latter being shown in the same sectional view as FIG. 4; and

FIG. 6 is a front elevational view of the electrode and dish of FIG. 5, the dish being shown in sectional view taken along the line 6—6 of FIG. 1.

Referring now to FIGS. 1 to 4 inclusive, the embodiment of the invention shown is particularly adapted for use with a pair of dipping electrodes both of which are cylindrical at the ends thereof intended to contact a sample solution, one being truncated by a plane, the other being truncated by a concave face. In the form shown, the device of FIG. 1 is a generally block-shaped element 20 having upper surface 22, lower surface 24, and side surfaces 26, 28, 30 and 32. Upper surface 22 includes three depressed portions 34, 36, and 38 all arranged contiguously with one another along a common axis. The depressed portions therefore have a common upper edge or lip 40 defined by the intersection of their surfaces with surface 22. Element 20 preferably is formed of water-insoluble, imporous, chemically inert (at least to the sample solutions with which it is intended to be used) material, typically glass or a synthetic polymer such as polyvinylchloride which can be easily molded or cast.

Depressed portion 34 is substantially scoop-shaped, having its back wall 42 concavely curved, substantially cylindrically, with a radius of curvature somewhat larger than is necessary to have the wall conform to the cylindrical end of a dipping electrode of the type described hereinafter. Front wall 44 of portion 34 is a substantially plane surface sloping at an angle α from a front section of lip 40 to meet the lowest or deepest extremity of wall 42 at an angle to the latter established approximately by the conical angle of the electrode end to be fitted therein. Thus, in section transverse to the common axis, as shown in FIG. 4, portion 34 appears similar to a scoop, back wall 42 meeting surface 22 at an angle so that a rear section of lip 40 formed by the intersection of wall 42 and surface 22 is a hemi-oval curve. The intersection of

surface 22 and wall 44 is of course a straight line which is preferably parallel to the common axis of the depressed portions.

Portion 36 is similarly scoop-shaped, having its back wall 46 concavely curved, substantially cylindrically or conically, with a large enough radius of curvature to conform loosely to a correspondingly cylindrical or conical end of an electrode. The front wall 48 of portion 36 is a substantially plane surface sloping from the front section of lip 40 to meet the bottom of the trough configuration of portion 36. This is shown in the section of FIG. 2 wherein it will be seen that back wall 46 and front wall 48 meet at an angle determined by the conical angle of the electrode and intended to be inserted in portion 36, i.e. the plane of wall 48 is normal to the axis of symmetry of wall 46. Front wall 48 intersects surface 22, along a line substantially parallel and preferably colinear with the line of intersection of front wall 44 of section 34 with surface 22. Importantly, front wall 48 slopes at the same angle α with respect to surface 22 as front wall 44.

Positioned substantially centrally in front wall 48 is a small protuberance or teat 50 which, as will be explained, serves as a stirrer, and is shorter than the depth of the concave face of the electrode.

Depressed portion 38 is merely a trough or canal which is disposed to provide fluid communication or a path between portions 34 and 36 and therefore opens into both the latter.

The operation of the present invention is advantageously described in conjunction with a pair of known electrodes readily available commercially. For example, referring to FIGS. 4 and 5 there will be seen a pair of electrodes 52 and 54 mounted in operative relation to the dish of the present invention. Electrode 52 is a typical calomel reference electrode and characteristically its electrically active exterior is at cylindrical end portion 56. Electrode 54 is a typical electrode of the type having its active end formed as cone 58 having a dished or concave truncation 60. This structure is a divalent ion-sensitive electrode is similar to that hereinbefore referred to in the aforesaid application Ser. No. 559,466.

In the usual manner, electrodes 52 and 54 are mounted in side by side relation as in FIG. 6 preferably with the extreme ends of truncation 60 and end portion 56 in coplanar relation. Thus, end portion 56 of the reference electrode can be fitted into depressed portion 34 of dish 20 whilst simultaneously, truncation 60 of the ion-sensitive electrode is fitted into depressed portion 36. It will be seen that the depressed portions are dimensioned to be slightly larger than the corresponding electrode tips so that a small interspace is left through which sample solution can flow. Clearly, very small quantities of sample solution, e.g. 1 ml. or even less, suffice to fill such interspace and provide ionic communication between the electrodes while contacting the entire active surfaces of the electrodes.

In order to insure that air does not become entrapped with the concavity of truncation 60 or against the flat bottom of cylindrical end portion 56, it is preferred to mount the two electrodes so that their long axes form the angle α with respect to vertical (assuming surface 22 dish 20 is to be the horizontal). Thus, the bottom faces of the electrode ends are parallel to surfaces 48 and 44 when inserted into dish 20. The angle α is determined primarily by the edge angle of the concavity of truncation 60 of a particular electrode with which dish 20 is to be used. For example, if the portion of the concavity of truncation 60 (which is usually rotationally symmetrical about an axis which is colinear with the longitudinal axis of the electrode) adjacent an edge thereof forms an angle β with respect to that longitudinal axis, then α should be about the complement of β . Usually, β is between about 60° to 75°, hence α should lie in the range of about 15° to 30°. It will be apparent that if the electrodes are

mounted at angle α to the vertical, edge portion of the concavity of truncation 60 will be quite horizontal. If actually α is a few degrees greater than the complement of β , the edge portion of the concavity will slant upwardly from the horizontal. In either case, air bubbles in the concavity will tend to slide out or be easily removed. This can be effected simply by gently moving or shaking the dish and electrodes relative to one another that teat 50 can act as a stirrer and engage such bubbles or create eddies either of which will tend to force the bubbles out of the concavity of truncation 60.

While the present invention has been described in conjunction with a reference dipping electrode having a cylindrical tip shape, it will be obvious to those skilled in the art that the configuration of dish 20 can be modified to allow depressed portion 34 to conform to other tip shapes such as conical, spherical or the like.

Similarly dish 20 need not be a solid block but can be hollowed underneath in the portions thereof not depressed, thus reducing the amount of materials used. Although in the form shown, for the sake of stability, dish 20 includes bottom lip flange 62 surrounding the dish and substantially coplanar with bottom surface 24, the device need no such flange and indeed can be mounted in a number of other configurations (e.g. with legs) so as that surface 22 can be kept substantially horizontal when in use.

Since certain changes may be made in the above apparatus without departing from the scope of the invention herein involved it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A container for sample solution, ionic activity of which is to be determined by a pair of elongated dipping electrodes immersed therein, one of said electrodes being an electrode of the type having an end which is concavely dished, said container comprising, in combination;
 - a) an element having a top surface with at least two separated, depressed portions therein, each of said depressed portions having a forward wall in the form of a corresponding plane surface sloping downwardly in the same direction and at substantially the same angle from said top surface toward the depth of the respective depressed portion, each depressed portion having an arcuate back wall connected adjacent said depth to the corresponding forward wall; and
 - b) a channel in said top surface for providing a fluid path between said depressed portions.
2. A container as defined in claim 1 including a protuberance substantially centrally located in the plane surface of one of said depressed portions.
3. A container as defined in claim 1 wherein said angle is one in the range of from 15° to 30° from said top surface.
4. A container as defined in claim 1 wherein each plane surface is disposed at an angle approximately normal to the axis of symmetry of the corresponding back wall.

References Cited

UNITED STATES PATENTS

2,499,852	3/1950	Dietz	204—195.1
2,838,233	6/1958	Garrison	204—195
3,055,759	9/1962	Busby et al.	204—195
3,222,269	12/1965	Stanton	204—242

JOHN H. MACK, Primary Examiner

T. TUNG, Assistant Examiner

U.S. Cl. X.R.

23—253; 73—425.4; 206—2; 215—1; 204—279