Spherical Segment Mercury Drops of Variable Size: The BAS Controlled Growth Mercury Electrode

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The drop sizes attainable with the BAS controlled growth mercury electrode were characterized by linear sweep voltammetry. The drops formed are considered as spherical segments, the height of which can be varied by altering the valve opening time. At slow potential scan rates, the drops with a small meniscus exhibited microelectrode behavior.

The BAS controlled growth mercury electrode (CGME) system uses a large bore capillary (150 μm) with mercury flow regulated *via* a fast response valve actuated by a computer generated pulse sequence [1,2]. Very short valve opening times offer the possibility of attaining renewable mercury microelectrodes. Such a system offers considerable advantages for *in situ* measurements in natural waters [3]. There have been few attempts to fabricate such an electrode to date [4,5]. The BAS CGME is the first to be commercially available. The range of mercury drop geometries and sizes attainable with this system are determined in this work.

Experimental Procedures

All measurements were performed with a BAS 100B/W electrochemical workstation coupled with a BAS CGME controlled growth mercury electrode. An Ag/AgCl reference electrode and a Pt wire auxiliary electrode were used.

The glass capillary was silanised to prevent retraction of mercury and irreproducible drop formation. This was effected by standing the capillary tip in a dimethyl dichlorosilane solution (5% v/v in carbon tetrachloride) for 15 min. Excess solution was aspirated from the capillary which was then dried overnight at 60°C.

Measurements were performed in glass voltammetry cells, and all solutions were purged with nitrogen (oxygen-free) for at least 15 min. prior to analysis. Solutions were stirred with a Teflon-coated magnetic stirrer bar.

All solutions were prepared in deionized water. Metal solutions were prepared from the nitrate salts (BDH, Analar); KNO_3 was from Merck (Pro Analysis), acetate buffer was prepared by mixing equal molar concentrations of acetic acid (Ajax, Univar, AR) and sodium acetate (Prolabo, Normapur, AR).

Results and Discussion

The magnitude and geometry of the mercury drops formed was characterized by linear scan voltammetric measurements for reduction of Pb(II) (10^{-4} M in 0.01 M KNO_3, scan 2 mV s^{-1} from -300 to -900 mV). The drops formed conform to a spherical segment geometry; as the valve opening time is increased, the height of the segment, h, increases, but the base (defined by the capillary bore) remains fixed. Electrode size may be calculated from steady-state limiting current (i_l) measurements, using the relationship:

$$i_l = knFcDr$$

where n is the number of electrons involved in the electrode reaction, F is Faraday's constant (96,485 C/eq), c is the bulk concentration of electroactive species, D is the diffusion coefficient, and r is the electrode radius [6]. The coefficient, k, has defined values for specific elec-

T1

Height, h, of the spherical mercury drop segment for selected valve opening times

| Valve Opening Times (ms)	k^a	h/r^b	$h(\mu m)$
20	4.1104	0.2299	17
30	5.2328	0.6965	52
40	6.7391	1.1001	83
50	10.1148	1.7999	135
100	11.4314	2.0569	154

[a]k calculated from $i_l = knFcDr$ (see text for details).

[b]ratio h/r interpolated from data reported by Stojek and Osteryoung (6); r = 75 μm (capillary bore radius).

F1

Current for reduction of Pb(II) as a function of (valve opening time)$^{2/3}$. Linear region of plot corresponds to spherical drop growth. Conditions: scan rate, 2 mV s^{-1} from -300 to -900 mV; [Pb(II)] = 10^{-4} M in 0.01 M KNO$_3$.
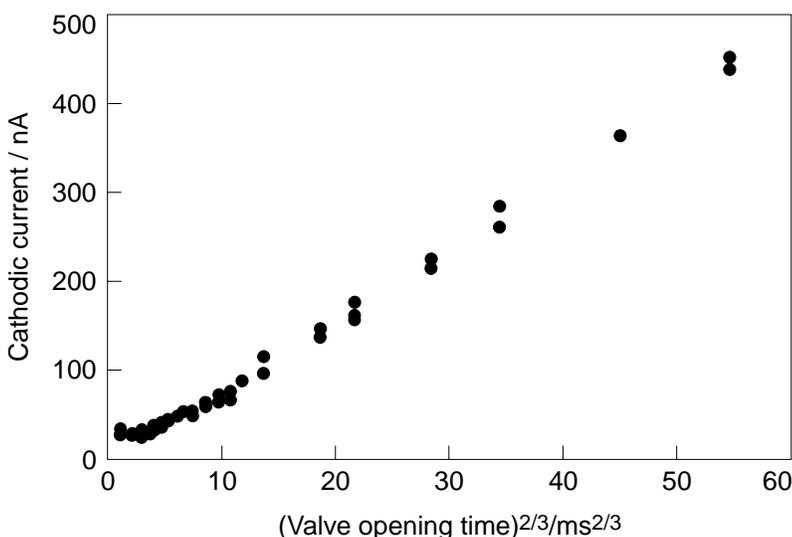
F2

*Current for reduction of Pb(II) at the smaller mercury drops as a function of (valve opening time)$^{1/3}$. Conditions as in **F1**.*
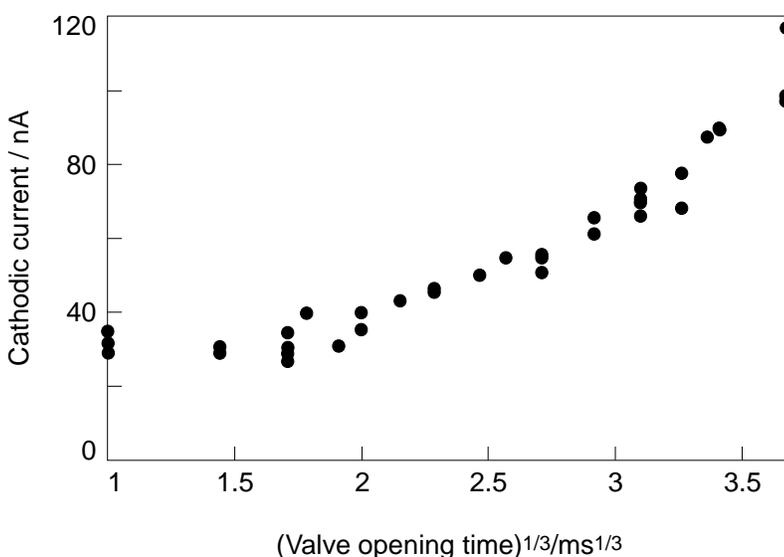
trode geometries, being 4.0 for a disk, 2π for a hemisphere, and 4π for a sphere [6]. The diffusion problem for intermediate spherical segment geometries is complex. Stojek and Osteryoung [6] have determined experimentally the dependence of the steady state current on the height of a spherical segment and reported k values for a range of h/r ratios. In the present work, k was calculated from the measured i_l for reduction of Pb(II) (c = 10^{-4} M) by substitution of appropriate parameters in the above equation (r = radius of the capillary bore (75 μm), D = 0.9 x 10^{-5} cm^2 s^{-1} (7), n = 2). This k value was then used to calculate h by interpolation of the published data (6). Results are given in **T1**.

Thus, the mercury drops formed by the CGME range from a meniscus to hemispherical and larger spherical segments. Stojek and Osteryoung [6] note that even for h = 2r, the electrode shape most closely resembles that of a hemisphere on a fixed plane, rather than a suspended sphere with a point of attachment.

Further information on the geometry of the mercury drops is provided by the dependency of the limiting current for Pb(II) reduction on the valve opening time, t. For spherical growth of a conventional sized drop, i_l is proportional to the electrode surface area, and hence to $t^{2/3}$ [7] (**F1**). For electrodes which exhibit microelectrode behavior, i_l is proportional to the square root of the electrode area, and hence to $t^{1/3}$ [8] (**F2**). Combined with the data in **T1**, **F1** and **F2** demonstrate the continuum of spherical segments which are attainable with the CGME by variation of the valve opening time.

The ability of a small meniscus mercury drop (t = 20 ms) to act as a microelectrode was investigated. Linear sweep voltammograms measured under steady-state conditions (radial diffusion) have a characteristic sigmoidal shape. Peaks appear in the voltammogram when
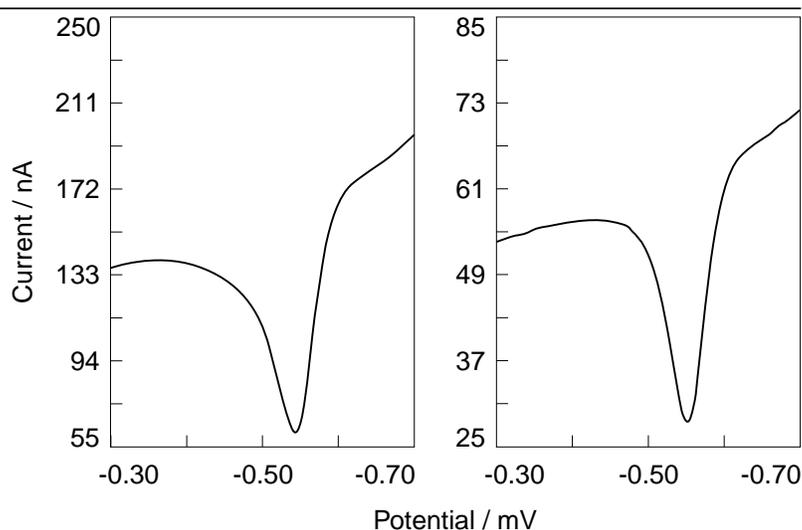
F3

Voltammetric curves for reduction of Pb(II) at a small meniscus mercury drop (valve opening time = 20 ms).

Scan rate: 1 mV s⁻¹ (—), 2 mV s⁻¹ (- - -), and 4 mV s⁻¹ (— · —). [Pb(II)] = 10⁻⁴ M in 0.01 M KNO₃.
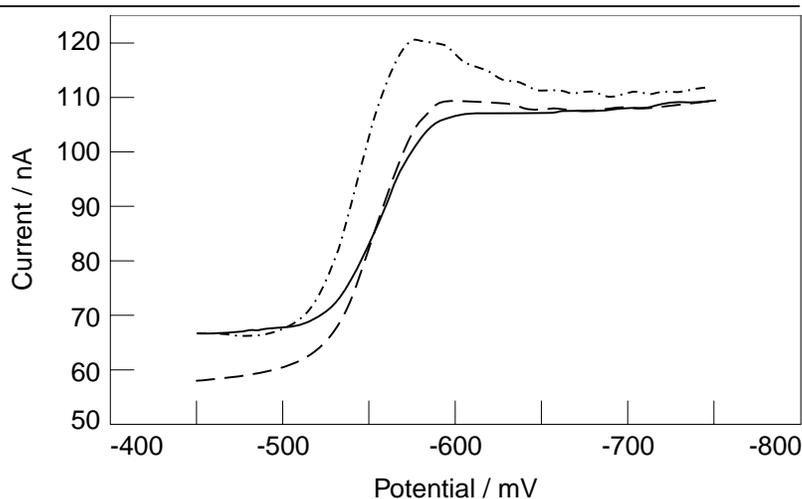
F4

DC-ASV stripping curves for Pb(II) obtained at valve opening times of 100 ms (LHS) and 20 ms (RHS). Conditions: deposition time, 300 s; deposition potential, -900 mV; pause before scan, 15 s; scan rate, 10 mV s⁻¹; stir speed, 400 rpm; [Pb(II)] = 5 x 10⁻⁷ M in 10⁻² M acetate buffer, pH 4.8.

is apparent at the larger spherical configuration (due to semiinfinite diffusion in the mercury drop).

Conclusion

The BAS CGME allows formation of mercury drops which conform to spherical segment geometry; the height of the segments is a function of the valve opening time. The smaller drop sizes available exhibit microelectrode behavior. This property, coupled with the ease of renewal of the electrode surface, are advantageous for studies on metal ion speciation in freshwaters (3).

Development of narrower bore capillaries may allow even smaller drops to be attained; the ability to function in an inverted configuration would be an added advantage (5).

Acknowledgment

References

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linear diffusion becomes significant. Typical results for reduction of Pb(II) are shown in **F3**; a sigmoidal curve is obtained at slow scan rates (≤ 2 mV s⁻¹), while a peak becomes apparent as the scan rate is increased.

Further evidence for microelectrode behavior is provided by DC anodic stripping voltammetry (DC-ASV) measurements. A plot of log (stripping current, i) *versus* log (potential scan rate, υ) has a slope of 1.0 for a very thin film [9], and 0.50 for a thick film [8]. DC-ASV measurements of Cd(II) (5 x 10⁻⁷ M in 0.01 M KNO₃) were performed using a range of potential scan rates in the stripping step (measurement parameters: deposition time, 180 s; deposition potential, -900 mV; pause before scan, 15 s). The ∂log i/∂log υ values obtained were: 0.99, t = 10 ms; 0.49, t = 50 ms; and 0.50, t = 200 ms. This clearly illustrates the thin-film characteristics of the meniscus electrode, the result for which compares very favorably with those reported by other workers for solid-state mercury film electrodes. For example, Wechter and Osteryoung [10] reported a ∂log i/∂log υ value of 0.846 for an Ir-based mercury film electrode (Ir wire diameter, 127 μm; Hg film thickness, 4.4 μm).

DC-ASV curves for measurement of Pb(II) (5 x 10⁻⁷ M in 10⁻⁴ M KNO₃) are shown in **F4** for t = 20 ms and 100 ms. At the meniscus drop, a symmetrical peak is obtained (consistent with film-like behavior); whereas significant tailing