A comparison between potentiostatic circuits with grounded work or auxiliary electrode

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Potentiostatic circuit configurations with work electrodes and auxiliary electrodes at ground potential have been reviewed and compared. Though the former is by far the best known and most used, the latter was more convenient and accurate in interfacial capacity measurements. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1463715]

I. INTRODUCTION

Potentiostatic circuits that employ operational amplifiers have been used routinely to apply a polarization potential to an electrode (usually referred to as a "work electrode") with respect to a reference electrode, avoiding the flow of any current through the latter, in order to keep it strictly nonpolarized. To this purpose, a third electrode, the "auxiliary electrode," is added to deliver the required current.

Potentiostatic circuits can exist in three different basic configurations, namely with grounded work (GW), reference (GR), or auxiliary (GA) electrodes, depending on which electrode is held at ground potential. Moreover, each configuration comes in two different flavors, depending on which electrode, the work or the auxiliary, is used to measure the current through the cell.

Two of the three basic configurations (GW and GA) are quite identical from an electrical point of view, while the third one (GR) is almost equivalent, as shown in the Appendix. Considerations of convenience usually suggest to choose one or another among them. The current measurement performed on one side or the other of the cell, instead, can affect, to a different amount, the accuracy of measurements, as it introduces the impedence of the current measuring device or circuit in series with the electrode it is connected to.

The GW configuration has been, by far, the most popular one and the one most frequently used [Fig. 1(a)]; the GR configuration [Fig. 1(b)] has been used mainly in multielectrode systems;[1] the third configuration, with the auxiliary electrode kept at ground potential, has received little attention and is seldom encountered in the literature. We are aware of only one work in recent years where this configuration is adopted or suggested.[2] This last configuration, however, offers some advantages over the classical one. Recently, we went through the whole subject in order to find an optimal configuration for the potentiostatic circuit to be used with the interfacial system we are currently studying. We did find that the GA configuration, though overlooked for such a long time, is indeed the most convenient.

II. EXPERIMENT

Currently we are using a potentiostatic circuit to polarize a sessile mercury drop electrode covered by a lipid monolayer. The apparatus is a modified Langmuir balance, by which surface pressure of the film can be measured by the axisymmetric drop shape technique while keeping the polarization of the mercury-monolayer-solution assembly at a constant controlled value.[3] An ac signal of given, small, am-

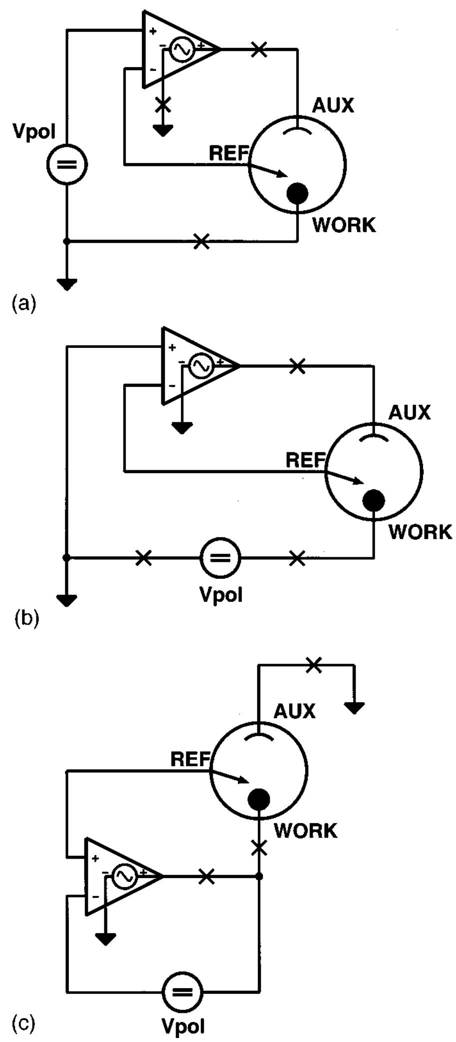

FIG. 1. The three basic configurations for potentiostatic electrode polarization: a: grounded work electrode (GW); b: grounded reference electrode (GR); and c: grounded auxiliary electrode (GA). The "X" marks the legs where electrode current can be measured.

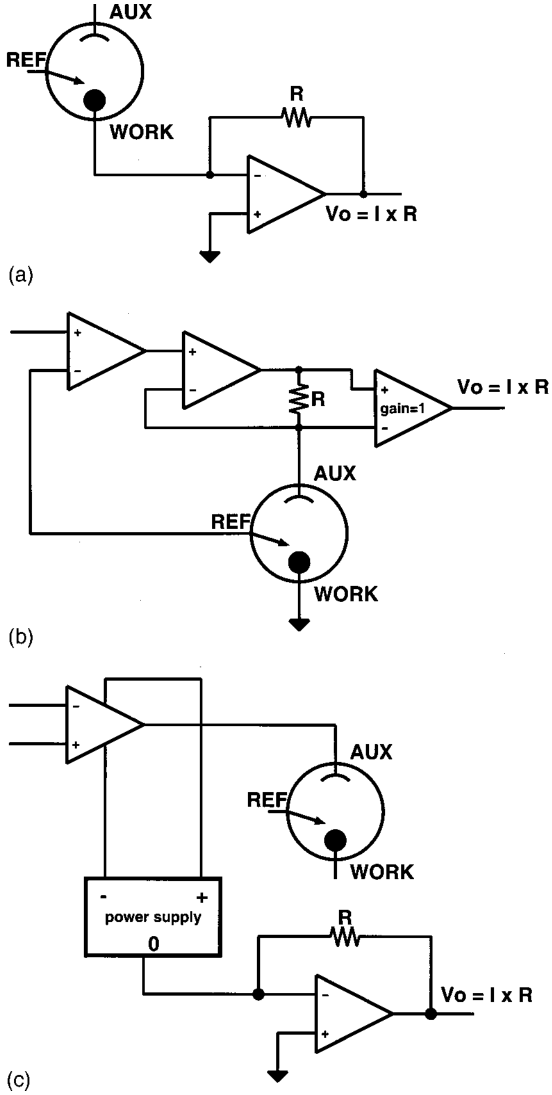

FIG. 2. Current measurement configurations with a current-to-voltage converter: a: ground referred converter; b: floating converter; c: current measurement from the power supply return terminal.

plitude is added to the polarization potential and, measuring with a lock-in amplifier the ac current flowing through the cell, the differential capacity of the assembly is obtained.

With the classical circuit of Fig. 1(a) some problem is encountered in measuring the current through the cell. One of the two usual arrangements, namely inserting a current-to-voltage converter (CVC) in series with the work electrode [Fig. 2(a)], is inconvenient in our case for two reasons: (i) The mercury electrode is connected to a mercury reservoir through tubing and the reservoir in turn is in contact with water as a piston liquid that through other tubings is pushed and pulled by motor burettes to increase or reduce the size of the drop. The whole assembly cannot be easily screened from external electromagnetic interferences; hence, if current is measured from the work electrode a lot of disturbances will be picked up. It is mandatory to effectively ground the work electrode for the range of frequencies of interest in order to short to ground these disturbances. (ii) Insertion of the CVC adds an impedence in series with the working electrode. This impedence is negligibly low at dc and in the

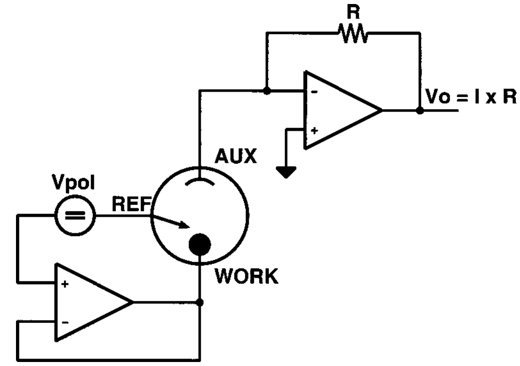

FIG. 3. Current measurement with the GA configuration.

range of very low frequencies, but it increases rapidly as the gain of the amplifier in the CVC rolls off with increasing frequency and, even worse, it behaves as an inductive reactance that results in series with the interfacial capacitance.

Current is more conveniently measured on the auxiliary electrode side of the cell, but this requires a ‘‘floating ammeter’’ or a power supply with a floating ground, as shown in Figs. 2(b) and 2(c), respectively. Both problems outlined in (i) and (ii) can be avoided without any increase in the circuit complexity using a configuration with the auxiliary electrode at ground potential, as shown in Fig. 3. The work electrode is connected to the output of a voltage follower whose very low output impedence contributes the shorting path to ground for the picked-up interference. On the other side, the CVC is implemented in the simple ground-referred configuration, with its spurious input impedence in series with the parasitic impedence of the auxiliary electrode, with no interference with the impedence of the interfacial system under study. The requirement for a floating generator for V_{pol} is naturally satisfied by the summing node that has to be introduced to superimpose the ac signal over the dc polarization voltage, as shown in the detailed schematic in Fig. 4.

The circuit can be implemented using cheap TL081 operational amplifiers for all functions. The results we report have been obtained using high accuracy OPA627 devices; the advantages given by this substitution are that no offset trimming is required up to an accuracy of 0.2 mV and a greater bandwith is available.

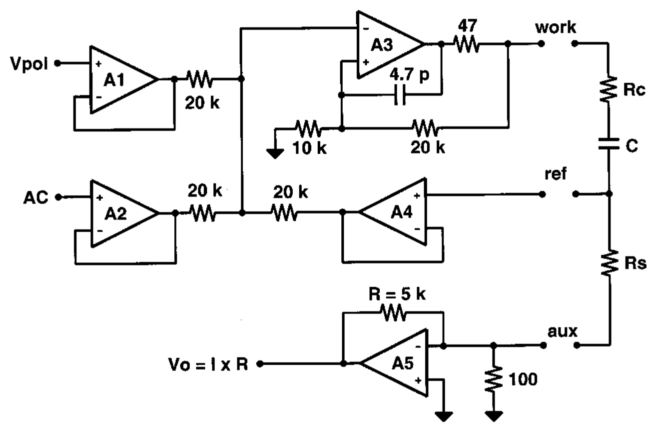

FIG. 4. Detailed schematic of the GA potentiostat. All Ai devices are OPA627.

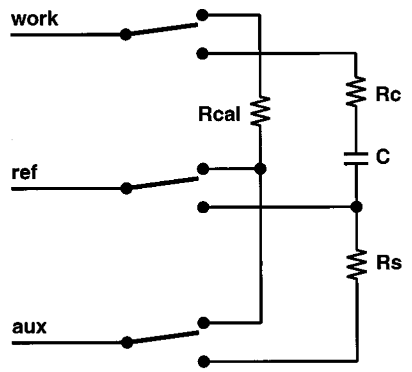

FIG. 5. The dummy cell used for test. $R_{cal}=16.2\Omega$; $R_s=5\Omega$; $R_c=15\Omega$; C as reported in Table I.

III. MEASUREMENTS

The circuit performance has been tested with the dummy cell shown in Fig. 5, whose values reflect our typical operating conditions. A calibration resistor with known value $R_{cal}=16.2\ \Omega$ has been employed instead of relying on the accuracy and stability of the lock-in amplifier generator; the magnitude and phase at the current-to-voltage converter output is measured with the calibration resistor (V_c) and with the cell (V_m). Then R_c and $1/j\omega C$ are obtained as the real and imaginary part of $Z=R_{cal}\cdot V_c/V_m$.

IV. RESULTS

The circuit has been tested for stability varying R_c and C; it resulted to be fully stable for R_c as low as 5Ω, with any value for C. The accuracy in capacity measurements has been tested, determining the useful frequency range for a given maximum error ($\pm0.5\%$). Results are reported in Table I. The third column in Table I shows the error that would be introduced by the insertion of the CVC in series with the work instead of the auxiliary electrode, at frequency $f=1$ kHz. At that frequency the input impedance of the CVC shown in Fig. 4 is equivalent to a 50 μH inductor, that is added in the GW configuration, in series with the unknown interfacial capacitor. The error introduced is quite small as long as the interfacial capacitor C is small ($\leqslant 2\ \mu$F), but increases rapidly for larger values of C.

TABLE I. Useful frequency ranges for a 0.5% maximum error for several capacity values. The third column shows the error that would be added by the CVC in the GW configuration at $f=1$ kHz.

C	Frequency range	Error at 1 kHz (GW configuration)
1 μF	50 Hz–16 kHz	0.2%
10 μF	25 Hz–4 kHz	2%
30 μF	20 Hz–2.5 kHz	6%

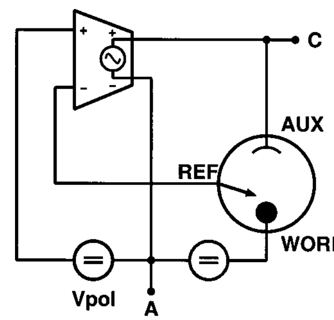

FIG. 6. Equivalence between GW and GA configurations (see the Appendix).

In conclusion, the GA configuration, though scarcely known and used in electrochemical work, should be preferred over the GW one whenever capacity measurement is involved.

APPENDIX

The equivalence of circuit 1a and 1c is immediately clear if they are redrawn as in Fig. 6, where the return path of the internal output generator of the operational amplifier is explicitly reported. Circuit 1a is obtained connecting node A to ground; circuit 1c is obtained connecting node C to ground and reversing the + and − signs both at the input and output terminations of the operational amplifier (which amounts, obviously, only to a change in notation with no effect on the circuit). In the latter case the V_{pol} generator is no more referred to ground, but must stay floating between the + output and the − input of the operational amplifier. Circuit in Fig. 1(a) is usually known as the negative feedback voltage amplifier, while configuration in Fig. 1(c) is best known as the "bootstrap circuit."[4]

The circuit in Fig. 1(b) is not exactly equivalent to the other two circuits in that the current flowing through the work electrode must also flow through the V_{pol} generator, while in case 1a and 1c V_{pol} is only a voltage reference with no current requirements. Circuit 1b can be obtained from 1a, as shown in Fig. 6, slipping the V_{pol} generator to the shadowed position.

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