Electrochimica Acta, 1966, Vol. 11, pp. 1147 to 1151. Pergamon Press Ltd. Printed in Northern Ireland

A NEW METHOD FOR THE COMPENSATION OF OHMIC DROP IN GALVANIC CELLS*

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Abstract—Generally the ohmic potential drop in a galvanic cell that occurs if a rectangular pulse is led through the cell, is compensated by means of a well-known bridge circuit. A better method making use of a phase reverter is described and its features are discussed. Exchange current densities up to 1200 mA/cm² can be studied. The error arising from mis-compensation of the ohmic drop does not exceed 5% in that case.

Résumé—Généralement on compense la chute ohmique qui se produit en faisant passer une pulsation rectangulaire dans une cellule galvanique du circuit de pont bien connu. Une meilleure méthode, qui fait usage d'une amplificateur paraphase, est proposée et ses caracteristiques sont décrites. Suivant cette méthode, on peut étudier des densités de courant d'échange jusqu'à 1200 mA/cm². Dans ce cas l'erreur produite par une non-compensation de la chute ohmique ne dépasse pas 5%.

Zusammenfassung—Im allgemeinen wird der Ohmschen Spannungsabfall, der entsteht wenn man einen Rechteckimpuls durch eine galvanische Zelle schickt, durch Anwendung einer Brückenschaltung kompensiert. Eine bessere Methode, wobei man einen Umkehrverstärker benutzt, wird beschrieben und die Vorzüge besprochen. Mit dieser Methode ist es möglich Austauschstromdichten bis 1200 mA/cm² zu untersuchen. Die Fehler, verursacht durch falsche Kompensation des Ohmschen Spannungsabfalls, sind kleiner als 5%.

INTRODUCTION

COMPENSATION or evaluation of the ohmic drop of a cell is one of the limits encountered in the study of electrode reactions with the galvanostatic single and double pulse methods.[1] In these methods it is preferable to use high concentrations of the electroactive species to minimize the influence of concentration polarization. In the case of fast reactions the exchange current density, i_0, will be large and thus the transfer resistance, RT/nFi_0, small in comparison with the electrolytic resistance. The compensation of the ohmic potential drop has been performed until now with a bridge circuit described by Delahay,[2] Fig. 1.

The ohmic drop in the cell is indicated by a sudden voltage variation in the voltage/time response at the start of the pulse. If R_3 is equal to the ohmic resistance this jump disappears and the ohmic drop will be compensated.

It is necessary that the oscilloscope of Fig. 1 has an amplifier with a differential input and a sensitivity of at least 1 mV/cm. Differential amplifiers commercially available have a poor rise time (>1 μs), consequently compensation of the ohmic drop is difficult to perform with sufficiently high accuracy. The common mode rejection of these arrangements is always less than 40 db at the higher frequency range. This means that an ohmic drop of 50 mV cannot be compensated within 0·5 mV. Moreover these amplifiers are sensitive to saturation effects so that the common mode may not exceed a certain value. This is an especially serious drawback for double-pulse studies if a short high level pulse, to charge the double layer capacitance, is applied.

* Manuscript received 21 December 1965.

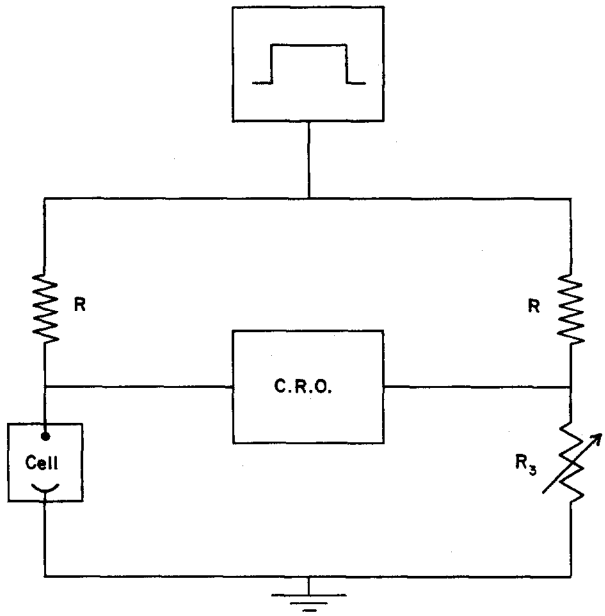

FIG. 1. Bridge circuit for compensation of the cell ohmic drop.

These disadvantages can be overcome if the ohmic drop is compensated by means of a circuit in which a phase reverter takes over the function of the differential amplifier.

CIRCUIT FOR COMPENSATION OF THE OHMIC DROP BY MEANS OF A PHASE REVERTER

The output of a pulse generator is connected with the grid of a triode, suitable for high frequencies, *eg* ECC 88. If the cathode and anode resistances are almost equal, both outputs have nearly the same amplitude but opposite sign. Such a set-up is known as a phase reverter.

One of the pulses serves as the galvanostatic current polarizing the cell, the other one is used to compensate the ohmic potential drop in the cell. The voltage measured by the oscilloscope will be

$$\eta = \eta_{el} + i_1 R_\Omega + i_1 R_3 - i_2 R_3.$$

If the sum of the last three terms is zero, the measured voltage equals the cell response compensated for the ohmic drop. From Fig. 2 it follows that the input of the C.R.O. may be asymmetric so that a fast-response amplifier can be used. Saturation of the amplifier is not likely to occur; only very short transients (<50 ns), due to reflexions, may do so.

The "common mode rejection" for this "semi-bridge circuit" has been tested by replacing the cell by the network of Fig. 3a, closely resembling the cell at high frequencies. The voltage response of this network was measured with and without compensation for the ohmic voltage drop across the resistor of 22 Ω. The compensated response was compared with the response of the same network without the series resistor of 22 Ω, Fig. 3b. From Fig. 4 one may conclude that the common mode rejection has been performed better than 60 db for pulse lengths longer than

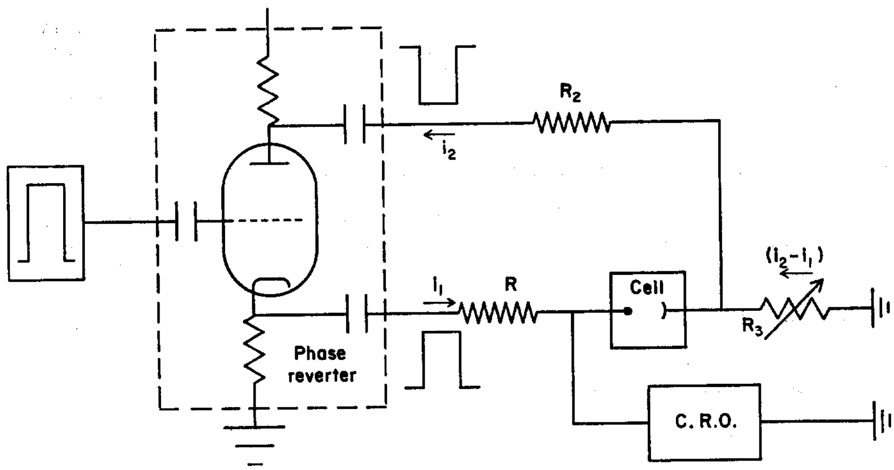

FIG. 2. "Semi-bridge" circuit for compensation of the ohmic drop in galvanostatic pulse methods.

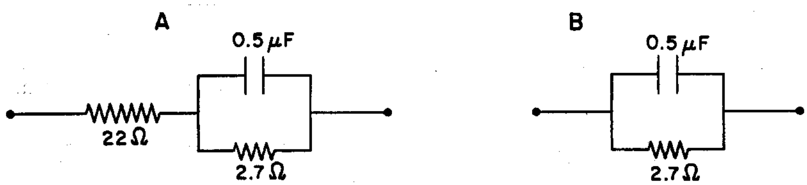

FIG. 3.

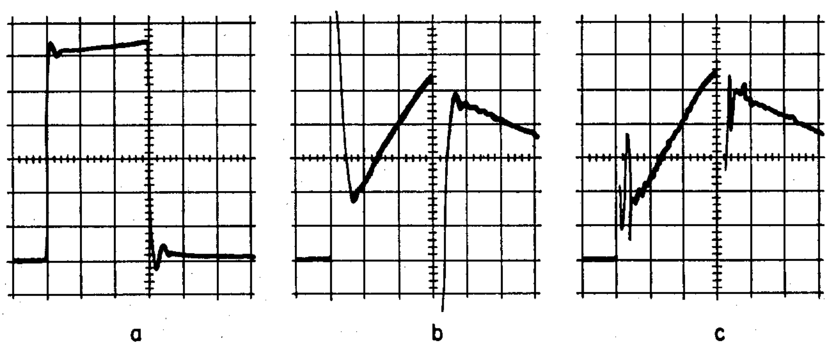

FIG. 4. Tracings of potential/time curves for
(a) Network of Fig. 3a without compensation of the ohmic drop (voltage scale 20 mV/cm).
(b) Network of Fig. 3a with compensation of the ohmic drop (voltage scale 1 mV/cm).
(c) Network of Fig. 3b (voltage scale 1 mV/cm). Time base 0·2 μs/cm in all cases.

0·3 μs. The following apparatus was used: Hewlett–Packard HP 214 A pulse generator (rise time <20 ns); HP 140 A oscilloscope with plug-in amplifier HP 1402 A. The response was pre-amplified with a Tektronix 1121 pre-amplifier. Photographs were recorded with a Polaroid camera HP 196 B.

Relation between accuracy of ohmic drop compensation and highest attainable value of i_0

Even with good electronic design, short transients—due to unmatched impedances—such as those in Fig. 3 were observed at the start and the end of the pulse. If high current densities (>100 mA/cm^2) are applied to the cell, the ringing is damped only after about 0·3 μs and compensation of the ohmic drop cannot be performed

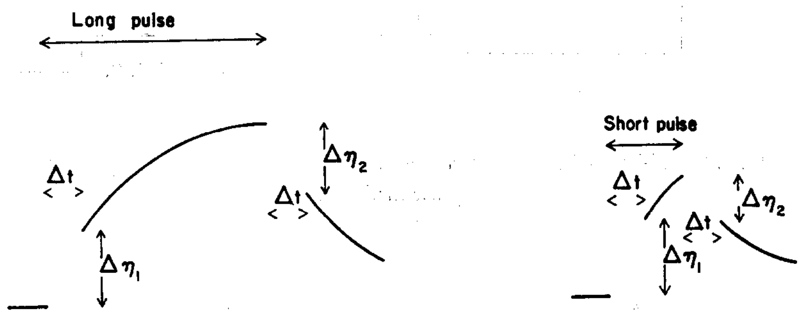

FIG. 5. Tracings of η/t curves for an RC combination. Transients, during Δt s, which obscure the response at the leading and trailing edges of the pulse, are not represented.

accurately. If high exchange current densities, exceeding 1200/n mA/cm^2, are studied, compensation of the ohmic drop will introduce errors larger than 5%. This can be illustrated as follows:

At short pulse lengths the electrode behaves almost as a transfer resistance $R_A = RT/nFi_0$ shunted by the double layer capacitance C_d. The voltage/time response of such a network, if a rectangular pulse during t_1 s is applied, is

$$\eta(t) = iR_A\left[1 - \exp\frac{-t}{R_AC_d}\right],\ 0 < t < t_1, \tag{1a}$$

$$\eta(t) = -iR_A \exp\frac{-t}{R_AC_d}\left[1 - \exp\frac{t_1}{R_AC_d}\right],\ t > t_1. \tag{1b}$$

From these equations it appears that $[d\eta/dt]_{t=t_1} < [d\eta/dt_1]_{t=0}$. So it is better to compensate for an ohmic drop at the trailing edge of the pulse. Further t_1 should be as short as possible, see Fig. 5.

The shortest pulse length to be applied is about 0·5 μs and the time Δt in which transients are damped is 0·3 μs. Let the value iR_A be 2 mV. Then a current density of 100 mA/cm^2 must be applied to the cell, if i_0 is 1200/n mA/cm^2. Inserting these values in (1b) together with the reasonable value of 25 μF/cm^2 for the double layer capacitance, one obtains $\Delta\eta_2 = 0{\cdot}7$ mV (note that $\Delta\eta$ for the leading edge is 0·9 mV). Extrapolation of the voltage/time response from $t_1 + \Delta t$ to t_1 introduces an error of probably less than 0·1 mV. Thus $iR_A = 2$ mV can be determined with an accuracy of 5%.

At larger values of i_0, $\Delta\eta$ will be more than 0·7 mV and the inaccuracy of ohmic drop compensation will be more than 5%. Note that the highest measurable value of i_0 strongly depends on Δt and consequently on the bandwidth of the amplifiers used in the set-up. As differential amplifiers always have narrow bandwidth as compared with asymmetrical amplifiers, the set-up proposed in this paper is evidently superior to the bridge method.

REFERENCES

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2. T. Berzins and P. Delahay, *J. Am. chem. Soc.* **77**, 6448 (1955).