2. Studies on the Controlled Potential Electrolysis. (V)

A New Automatically Controlled Apparatus

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INTRODUCTION

Controlled potential electrolysis is a promising method for quantitative separation and determination of elements, for syntheses of both organic and inorganic compounds and for plating metals *etc*.

A number of literatures has been published since Haber[1] first introduced this technique and the applications. Previously, the authors reported on the controlled potential electro-analysis, its automatic apparatus and its applications to the electrolytic gravimetry and to the polarographic analysis.[2]

Recently, with the progress of polarography and of instrumentation, the value of controlled potential electrolysis has come to be recognized again and the recent progress was reviewed by the authors.[3] Many designs of potentiostat have already been reported,[4-12] which automatically performs the function of maintaining the potential of a working electrode constant during the electrolysis.

Lingane and Jones[4] described the potentiostat composed of galvanometer-switch, dual relay and a reversible motor. An analogous instrument was reported by the authors[2]. Caldwell, Parker and Diehl[5] used direct current amplifier instead of galvanometer-switch,. Penther and Pompeo[6] employed the Brown converter and amplifier and thereby produced direct current was introduced to the saturable reactor which regulated the electrolysis current. Hicking[7] and Chamber[8] constructed all electronically controlled apparatus having no moving part. Greenough, Williams and Taylor[9] and recently, Oka, Muto and Nagatsuka[10] used multivibrator circuit for the same purpose. Lamphere and Rogers[11] applied the Brown converter and amplifier to operate the reversible motor for controlling the electrolysis current. Allen[12] constructed extremely sensitive potentiostat using amplidyne generator for the same purpose. These instruments were recently reviewed by Muto[13].

In this paper, a new sensitive potentiostat employing galvanometer-switch and reversible motor is described. This instrument is completely line-operated from 110 -volt alternating current source except one 1.5 volt dry battery for reference potential, and the senstivity to the change in electrode potential is about ± 7 millivolts.

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APPARATUS

A block diagram of the apparatus is shown in Figure 1. This apparatus is similar

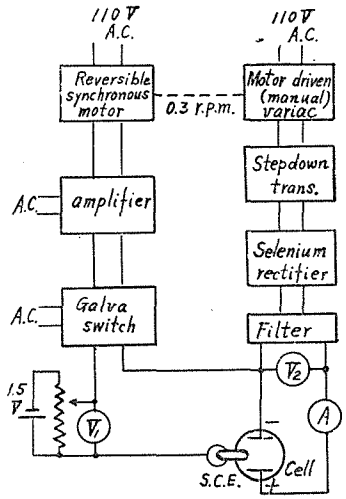

Fig. 1. Schematic circuit.

to that previously reported[2], but some improvements were made. The chief one is the use of simple alternating current amplifier instead of the magnetic relay in the latter apparatus and in this time rectified current is used for electrolysis power source. The power supply is composed of a motor driven Variac transformer which is also controlled manually without any preliminary operation, a step down transformer, selenium rectifier and inductance-capacitance filter circuit to smooth the rectified direct current. A voltmeter and a two range ammeter indicate the total voltage applied to the cell and the electrolysis current respectively. The main parts of the control circuit are a simple potentiometer powered by a 1.5 volt dry cell to provide the reference voltage, a sensitive galvanometer-switch which supplies the opposite phase alternating current potential to the power amplifier tube 6V6 according to the galvanometer deflection, and reversible synchronous motor (Oriental Synchronous Motor, 1 watt, 1800 r.p.m.) which follows the amplifier and controls the Variac automatically. When the potential of the working electrode against the reference electrode (usually a saturated calomel electrode) differs from the opposing reference voltage, operate the Variac in the appropriate direction until the potential of the working the galvanometer-switch makes contact right or left which causes the motor to electrode returns to the value of the reference voltage. As the reference voltage is read directly on a meter, the control circuit requires no preliminary adjustment or calibration before use.

The complete circuit of the instrument is shown in Figure 2. Figures 3 and 4 show the total arrangement. As shown in Figure 2, power is drawn from the 110 volt 60

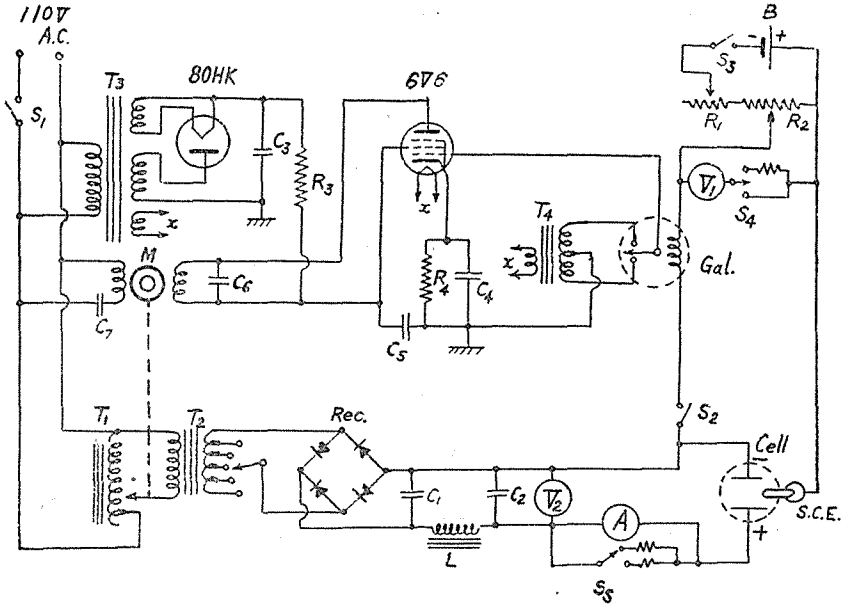

Fig. 2. Complete circuit.

A : Ammeter (200 and 2000 ma.)

B : Dry battery (1.5 or 3.0 volt)

C_1.C_2 : Electrolytic capacitor (12000 μfd.)

C_3,C_4,C_5 : Electrolytic capacitor (50 μfd.)

C_6 : Paper capacitor (2 μfd.)

C_7 : Paper capacitor (1 μfd.)

L : Choke (30 millihenry)

M : Oriental synchronous motor

R_1 : Potentiometer (1000 ohms)

R_2 : Potentiometer (1000 ohms)

R_3 : 430 ohms

R_4 : 1000 ohms

S_1,S_2,S_3,S_4,S_5 : Switch

T_1 : Variac autotransformer (0-130 volts, 3 amperes)

T_2 : Stepdown transformer (ratio : 100 to 25, 20, 15, 10 and 5)

T_3 : Power transformer

T_4 : Transformer (ratio : 6 to 10)

V_1 : Voltmeter (1.5 and 3.0 volts)

V_2 : Voltmeter (30 volts)

Rec : Selenium rectifier (3 amperes)

S.C.E : Saturated Calomel electrode

Gal : Galvanometer-switch

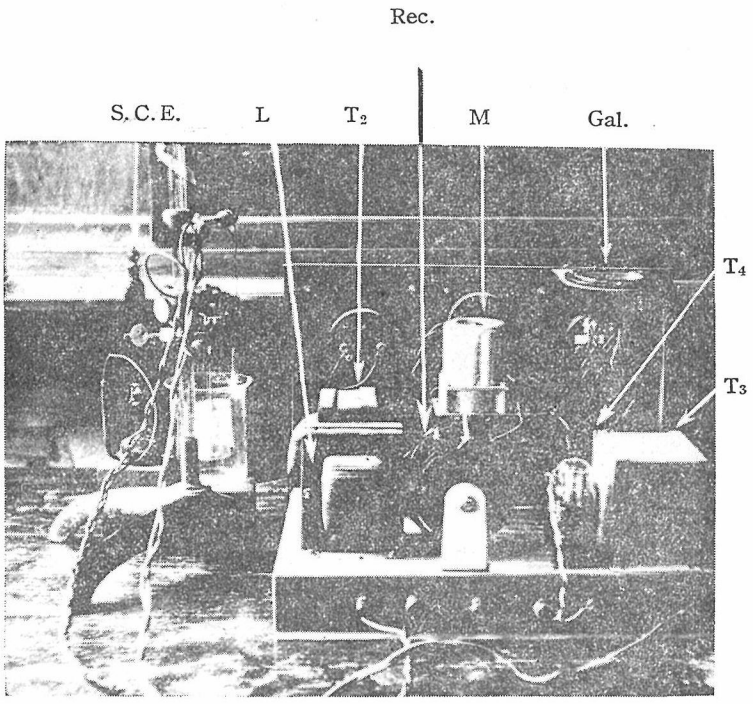

Fig. 3. Assembled unit (backward).

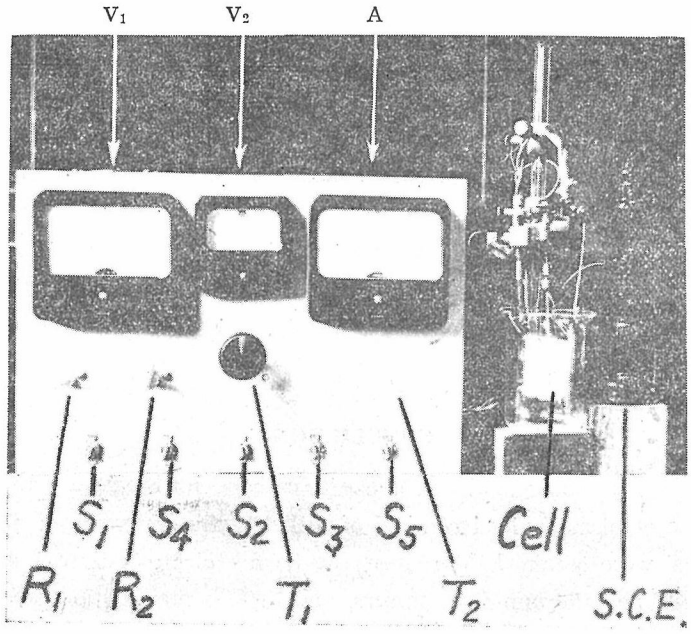

Fig. 4. Front view of the instrument.

cycle line and goes through the regulating variac T_1, which serves to vary the applied potential as dictated by the control circuit so as to hold constant solution-cathode potential in the cell. It is driven by the reversible motor at 0.3 r.p.m. reduced through a worm gear and a friction clutch. The clutch permits a quick setting to be made by hand at any time. Following it, a range control transformer T_2, is used to set the upper limit of direct current voltage obtainable from the regulator. It is abvisable to set this only a little higher than the maximum applied voltage expected during the electrolysis in order to reduce the voltage per turn on T_1. The meter V_2 and A read applied voltage and electrolysis current respectively. A range switch with two resistors provides the range of 200 ma. and 2000 ma. for A. The regulating system is composed of the potentiometer, galvanometer-switch, amplifier and the reversible motor. The working electrode-reference electrode potential is balanced against a reference voltage set up on the potentiometers R_1 and R_2. V_1 gives a voltage reading and has full scale range of 1.5 and 3.0 volts. If the cathode potential differs from the reference voltage, a small current flows through the galvanometer-switch circuit and the galvanometer-switch contacts to either direction. The alternating current voltage thus produced is amplified and causes T_1 to rotate in a direction that corrects the error. The circuit responds to a ± 7 millivolts difference and the galvanometer current is less than 10 micro-amperes, a value small enough to prevent polarization of the reference electrode and error due to *iR* drop.

OPERATING PROCEDURE

The electrolysis cell is connected to the apparatus in the usual way and the range control transformer T_2 is set a little higher than the maximum applied voltage expected during the electrolysis and the regulating variac T_1 is set to the minimum voltage and the switch S_3 is closed first and R_1 and R_2 are adjusted until V_1 indicates the cathode potential which is desired to maintain. Then S_1 and finally S_2 is closed to activate the control circuit and the apparatus is left to itself until the electrolysis is completed, because the subsequent operation is completely automatic. At the end of an experiment, S_2 should be opened to disconnect the control circuit before S_1 and S_3 are opened.

CONCLUSION

Tests were made using platinum gauze as cathode for the determination of copper in the presence of bismuth, lead *etc.* and of nickel in the presence of zinc; the satisfactory results were odtained. Moreover, the former electrolysis was also tested by using thorium-C and thorium-B as tracers, and little contamination was observed in the copper deposit. The ripple of cathode potential due to the rectification was observed by cathode-ray oscillograph, but the maximum ripple voltage was smaller than 4

millivolts at the above-mentioned electrolysis. The detailed results obtained will be discussed later.

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