JOURNAL OF APPLIED ELECTROCHEMISTRY 13 (1983) 371–376

Test cell simulating the operating conditions of water electrolysers for the evaluation of gas evolving electrocatalysts

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Received 26 July 1982

To evaluate promising anode, cathode, and separator materials in conditions similar to those present in a full-size water electrolyser, a test cell with electrode area of $10\,cm^2$ was constructed. In order to operate with current densities as high as $1\,A\,cm^{-2}$ a 10 A pulsed galvanostat was developed and built which features a 'sample-hold' circuit to measure the IR-free electrode overvoltages and direct meter readings.

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1. Introduction

It would be prohibitively expensive to evaluate all candidate anode and cathode materials by tests in a full-size electrolyser. Thus, reliable laboratory cells are required for assessing materials under conditions of prolonged hydrogen or oxygen evolution. A test cell has been developed for this purpose. The cell design seeks to simulate closely the conditions in a full-size electrolyser. Areas, $10\,cm^2$, of the anode and cathode materials are exposed to the electrolyte in this cell and potentials are measured with respect to reference electrodes.

Three variables are commonly encountered during electrode characterization measurements for water electrolyser research at constant temperature and solution composition. The electrode potential, V, the current density, I, and the time, t. Since we are interested in long term performance, the discussion is restricted to steady-state situations.

To minimize the operating cost of an electrolyser, it is important to minimize the overvoltages necessary to drive the O_2 and H_2 evolution at reasonable current densities $(0.5–1\,A\,cm^{-2})$.. At such high current densities it is necessary to separate any ohmic potential drop from the measured potential difference between the test and reference electrodes.

The steady state is usually attained after a short time (less than 1 min) but in water electrolyser research, much longer times are required. Our galvanostat allows the direct recording of the potential free of ohmic drop as a function of time and determines the steady state potential in a reproducible manner. The literature reports many devices, some quite useful in research and development laboratories. However, most of those instruments are complex, use an oscilloscope, and are not suitable for rugged performance conditions. Furthermore, they require highly skilled personnel for interpretation of the measurements.

2. Test cell

The test cells commonly developed have electrode areas of only $1\,cm^2$ for both cathode and anode. The test cell developed here has an exposed area of $10\,cm^2$ for both electrodes. This cell simulates a real size electrolyser more closely, since bubble formation and gas motion are important factors that have to be considered in the design of the electrodes. The cell also has, as in a practical size electrolyser, a separator which keeps the gases apart since the diffusion of O_2 gas or H_2 gas into the complementary electrode affects the electrode processes.

The cell module consists of three removable

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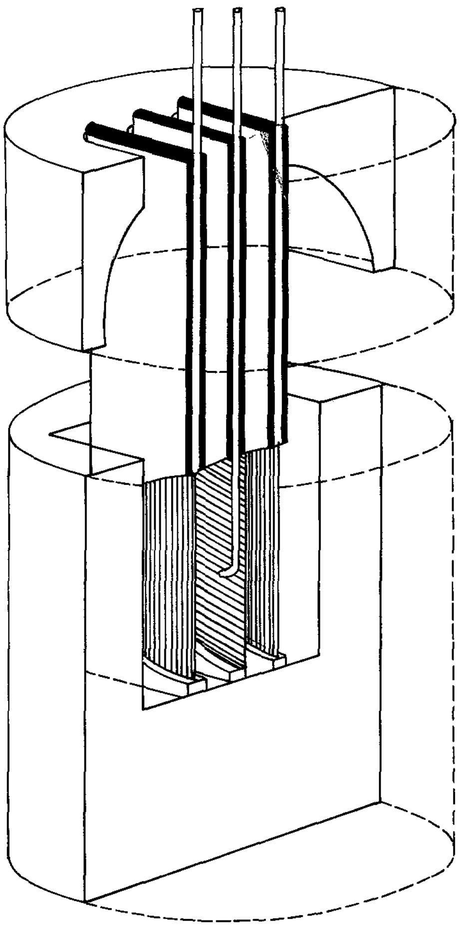


Fig. 1. Schematic view of the experimental cell. The module consists of three removable plug-in units which support electrodes and membrane.

plug-in units as shown in Fig. 1 and 2. Two of them carry the electrodes and a third one supporting the separator membrane. The cell frame and the plug-in are made of Teflon. The total electrode gap is 4 cm. The cell is thermostated, the counter electrode is platinum sheets soldered to a copper wire. The wire connection is insulated with silicone rubber. In order to simulate conditions similar to these existing inside an electrolyser, membranes with an area of 10 cm^2 were used. Experimental conditions were 80° C, 30% KOH. The electrolyte flows by thermal convection.

3. Pulsed galvanostat

In a typical galvanostatic measurement, a controlled current is forced between the working electrode (WE) and the counter electrode (CE) and the potential difference (PD) between the reference electrode (RE) and WE is measured with a high impedance voltmeter. By measuring this voltage for different current densities at the WE, it is possible to construct the Tafel plot for characterisation of the electrode catalyst. For a careful measurement of the Tafel plot, proper attention must be given to the ohmic drop between the WE and the RE. Since the path between the WE and CE is resistive the potential difference observed between them is the sum of the potential to drive the electrochemical reaction at a certain rate and the ohmic drop through the solution. Placing the RE as close as possible to the WE decreases the ohmic drop but does not solve the problem completely, principally at high density current. It is then necessary to separate the ohmic drop from the potential between the RE and WE. This is done by interrupting the current and measuring the potential difference immediately thereafter.

The initial, almost instantaneous, drop of V_{wr} (the potential difference between the WE and RE) with time is due to the ohmic loss. The slower decay of V_{wr} is due to the rearrangement of the double layer at the surface electrode.

To implement the pulsed technique described above two systems are normally used:

System A; if only a slow current source is available, the interruption of the current has to be done with a relay activated manually, the time evolution of the V_{wr} has to be recorded with a storage oscilloscope or with a buffered fast potentiometric (y, x, time) recorder. In this method a normal oscilloscope cannot be used since the current source cannot be chopped at the appropriate rate. However, mechanical switching proved to be inadequate for high current density; contact bouncing sometimes causes erroneous meter readings.

System B; if a more sophisticated current source with a rise time in the ms range is available, it is possible to switch the current source on and off with a pulse generator. Cutting off the current at a convenient rate, the time evolution of V_{wr} can be displayed on a normal oscilloscope triggered by the pulse generator.

All of the above schemes have to be used by a technician with some training in electronics and

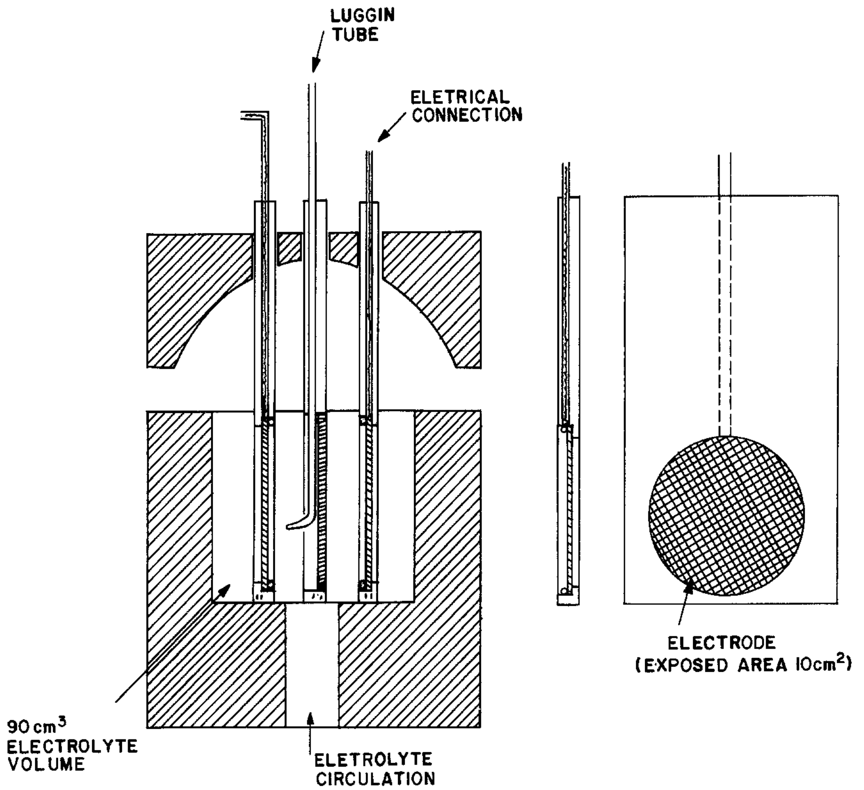


Fig. 2. Cross sectional view of the experimental cell.

the precision of measurement is at the best 40 mV, for a measured value around 1 V.

Considering the cost of the equipment described above and the technical limitations of some operators, we designed low cost simple to operate equipment to measure the electrode potentials free of ohmic drop.

The equipment, which is shown schematically in Fig. 3, is self-contained and has a built-in voltage measurement circuit connected to a

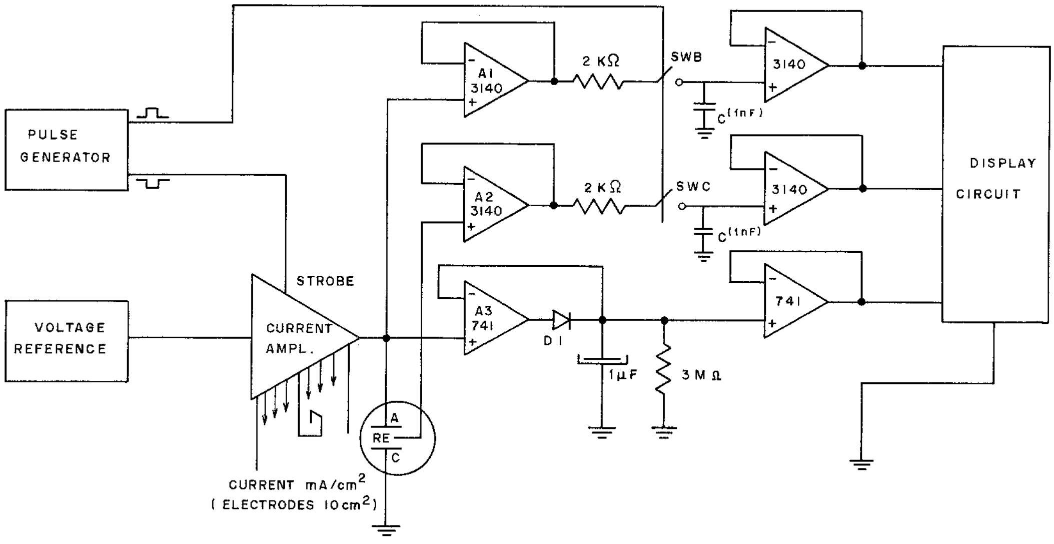
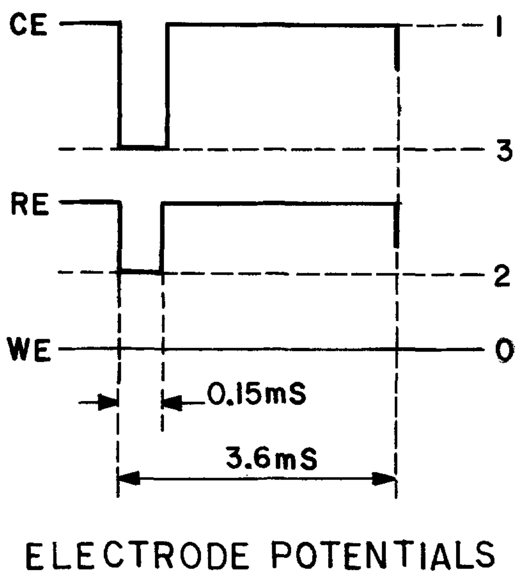


Fig. 3. Schematic diagram of the 10 A pulsed galvanostat.



	b			
	0	2	3	1
a				
0	–	–	–	–
2	*E* cathode	–	*E* anode	–
3	*E* cell	*E* anode	–	–
1	*U* cell	–	*IR* cell	–

Fig. 4. Diagramatic representation of the voltage measurement circuit, $V_{ab} = V_a - V_b$.

display. It measures the voltage V_{ab} which can be the WE potential, the CE potential, the IR-free potential E across the cell, the RI drop and, the total potential U applied to the cell, depending on the values of a, b selected in the front panel as shown in Fig. 4. In this way, for example, if we have $a = 2$ and $b = 3$ we are measuring the IR-free anode potential. Figure 3 shows the circuit diagram of the test instrument, it consists basically of 4 main circuits:

A pulse generator which generates pulses to switch the current amplifier on and off and to trigger the 'sample-hold' circuit. It generates pulses of 150 μs wide, every 3.6 ms. The pulse width was chosen to be 150 μs because in this time a complete cut-off of the power transistor is possible and this time is not enough to modify the double layer at the electrode surface substantially.

(1) The repetition rate of 3.6 ms was chosen arbitrarily but it is much longer than the interrupting pulse which makes the interruption practically insignificant. A pulse frequency which is too low causes deviation due to recuperation effects during the 'off' time; too high frequencies introduce capacitance errors.

(2) The current source is capable of switching from 10 A to zero in 1 μs. The current is driven to zero for 150 μs in each 3.6 ms.

(3) The 'sample-hold' circuit is formed by three identical circuits, one for the reference electrode and a second one for the working electrode and a third for the counter electrode. When the current is reduced to zero, simultaneously SWB and SWC are switched on, charging the capacitors to the electrode voltage. Operational amplifiers A1 and A2 insulate the capacitors, from the other electronic components since they have input impedance of 1 TΩ.

The A3 operational amplifiers, the D1 diode, the 1 μF capacitor and the 3 MΩ resistance form a peak storage in such a way that the measured value is the voltage applied to the cell with the current flowing and not its average value. The 'true' voltage of the chemical system is directly indicated on the display.

(4) The display circuit which converts the analog output of the shc to digital format appropriate to drive four seven segment displays.

The data obtained with our instrument have been checked many times against a precision square wave electronic switching instrument, no deviation could be detected.

In order to demonstrate the versatility of the instrument, examples of test results with different electrocatalysts are given in the following figures; in Fig. 5 the electrode potential for the oxygen evolution reaction referred to a Hg/HgO electrode are plotted versus the current density. The anode material used was nickel-plated steel and Teflon-bonded nickel–cobalt spinel ($NiCo_2O_4$) [1].

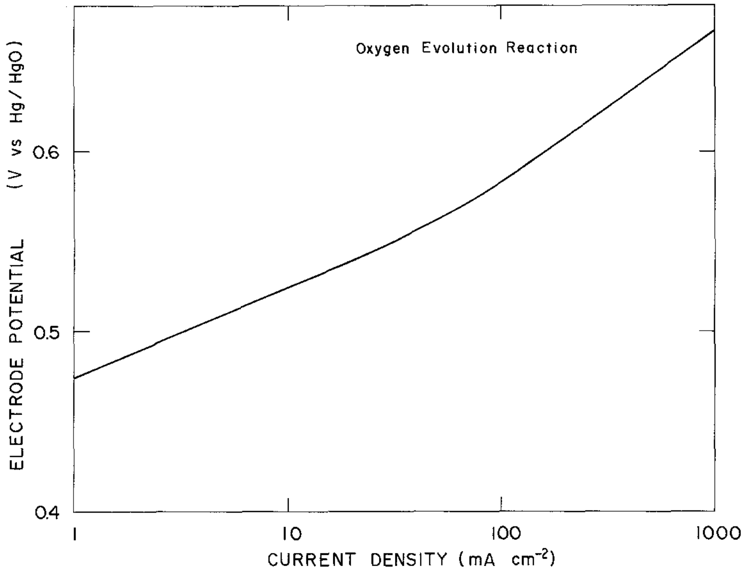


Fig. 5. Electrode potential versus Hg/HgO electrode for the oxygen evolution reaction. The electrode material is nickel-plated steel covered with Teflon-bonded nickel cobalt spinel.

The potential are referred to Hg/HgO electrode which is approximately 0.92 V versus the hydrogen electrode, as obtained by measurement in this investigation. The Tafel plot for the oxygen evolution reaction on the test electrode were determined using steady-state potentiostatic methods. The electrode was preanodized at a constant current of 1 A cm^{-2} for 30 min. Experiments were conducted at 80° C in the direction of high current to low currents. Ohmic free drop potential were measured directly using the electronic apparatus described above.

Figure 6 shows a plot of the electrode potential for the hydrogen evolution reaction referred to Hg/HgO electrode. The cathode material used was nickel-plated steel and Raney nickel [2]. The electrode was prepolarized at a constant current density of 1 A cm^{-2} for 30 min. Ohmic free potential drop were measured at 80° C in the direction of high current to low current. The reference electrode is Hg/HgO/aqueous solution of 30% KOH in all cases.

The electronic apparatus and the three-compartment cell have proved convenient to

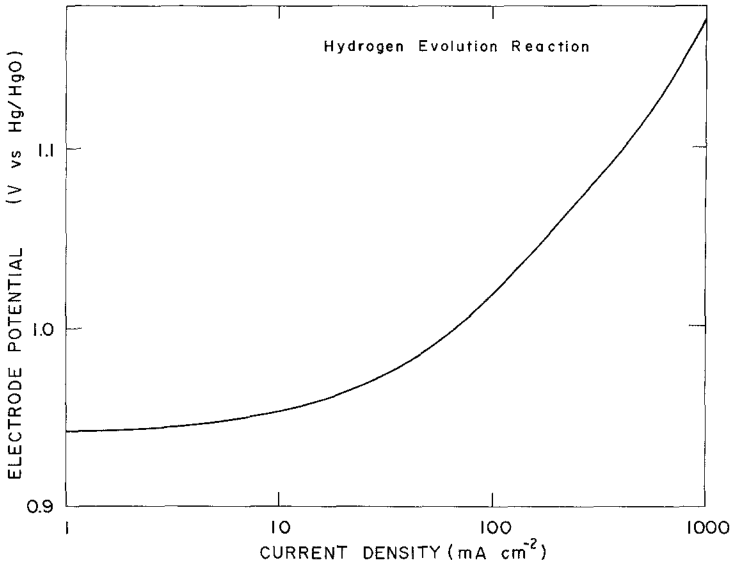


Fig. 6. Electrode potential versus Hg/HgO electrode for the hydrogen evolution reaction. The electrode material is nickel plated steel covered with Raney nickel.

measure the performance of electrodes at high current densities simulating conditions present in real size alkaline water electrolysers.

References

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