

THE EVALUATION OF WESTON CELL RELIABILITY ON THE BASIS OF THE ELECTROMOTIVE FORCE DRIFT

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The Weston cell, invented by Edward Weston in 1893, is a wet-chemical cell that produces a highly stable voltage suitable as a laboratory standard for calibration of voltmeters and for the determination of the electromotive force. The use of Weston cell after a long-time period as a calibration tool has to be considered carefully taking into account the possibility of certain modification in time of its characteristic parameters. This paper attempts to evaluate the reliability of a 55 year old Weston cell in terms of its actual electromotive force, its voltage drift as well as the internal resistance.

Keywords: Weston cell, electromotive force, voltage drift, internal resistance

1. Introduction

In 1908, The London Conference on Electrical Units and Standards has adopted Weston standard cell as the international standard for the electromotive force (emf) determination. Three years later, in 1911, The National Bureau of Standards took the same decision. The voltage was mentioned to be 1.01830 V, considering a reference temperature of 20°C [1].

However, Weston cell voltage varies between 1.0183V and 1.0194V, depending on the specific cell design and it is highly stable over the time, with a drift of approximately 0.004 % of rated voltage per year [2].

The main disadvantage of Weston cells consists in their intolerance to any current drain, so that the measurements cannot be performed using an analogue voltmeter without compromising accuracy. Most manufacturers stipulate typically a drain current of no more than 0.1 mA. Consequently, the voltage of standard cells could only be measured with a potentiometric (null-balance) device where leakage current is almost null. Short-circuiting the cell and disturbing the Weston cells mechanically or thermally could also lead to irreversible cell damage [1].

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There are two different types of mercury standard cells developed for various calibration purposes, namely the saturated and the unsaturated ones. The saturated standard cells have the advantage of providing the greatest voltage stability over time, at the expense of thermal instability, their voltage drift being insignificant with the passage of time. As opposed to them, the unsaturated cells provide better thermal stability. This causes standard cells to function best in temperature-controlled conditions. Nominal voltage for a saturated cell is 1.0186 V, while for an unsaturated one the voltage is 1.019 V [3].

Vigoureux and Watts have studied the temperature effect on electromotive force in terms of performance, in a temperature range of -24°C to $+40^{\circ}\text{C}$ [2]. They established that the electromotive force reaches a maximum value at about 3°C and behaved adequately at -16°C . They have noticed that at temperatures starting from -18°C a freezing process took place gradually, being followed by a rapid decrease in electromotive force. At -24°C the electrolyte has been completely solidified and the electromotive force was approximately 12 mV, lower than the maximum value. The frozen cells resumed their normal behaviour when kept at room temperature for about a day but the cooling process increased substantially the internal resistance of the cells. Therefore, the known equation for the emf dependence on temperature changes between -20°C and $+40^{\circ}\text{C}$ [2].

Data provided by the cell manufacturer show a voltage of 1.01860 V at 20°C with a variation of no more than of 3×10^{-6} V, under the optimal conditions (no load, no vibrations, stirring or other perturbation and the cell maintained in a upright position). A Weston standard cell has a long thermal after-effect; in the aging process, the voltage will have a small decrease, while the internal resistance will increase slightly [3].

Although electromotive force is constant over long periods of time, the cells must be calibrated at every 12 months [2].

Usually, the Weston cell has the form of an H-shaped tube (Fig. 1).

The left leg of the tube forms the cathode and it contains mercury in contact with a paste of mercurous sulphate ($\text{Hg}_2\text{SO}_4 + \text{Hg}$). This half-cell is a reference electrode of second kind. The other leg contains an amalgam of cadmium (usually with weight percent of Cd) in contact with $\text{CdSO}_4 \cdot 8/3 \text{ H}_2\text{O}$ crystals, and acts as the anode of the cell. The electrolyte is a saturated solution of cadmium sulphate and the mercurous sulphate paste serves as depolariser. Platinum wires are sealed in order to serve as terminals for connecting the cell to the external circuit [4].

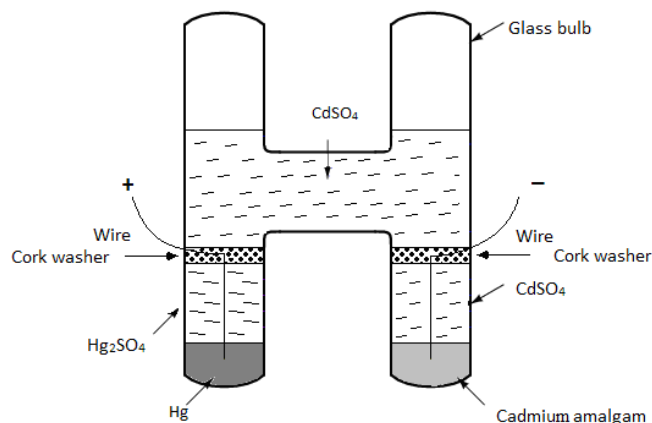
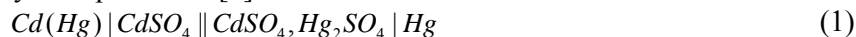
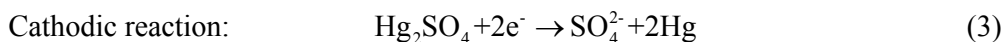
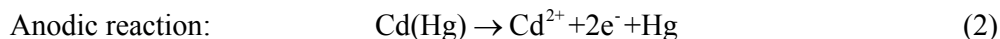


Fig. 1. A depiction of the Weston standard cell construction and its components

The above two electrodes, namely the amalgam electrode and the reference electrode may be represented [5] as follows:



The anodic and cathodic reactions taking place in a Weston cell are:



Standard cells are composed of two dissimilar electrodes immersed in an electrolytic solution. They are not intended to supply electric current; this is the reason why Weston cells have such a different design from electrochemical systems [6].

The terms saturated and unsaturated refer to the state of the electrolyte. The difference between the two types of cells is given by the use of an unsaturated solution of cadmium sulphate and the lack of $CdSO_4 \cdot 8/3H_2O$ hydrate crystals in the unsaturated type. The electromotive force value of the unsaturated cell at room temperature is about 0.05% higher than that of the saturated type [5].

American National Institute of Standards and Technology recorded Weston cells dating back 70 years, which are still stable [7].

The voltage is considered to be 1.01830V only at 20°C; for other temperatures the voltage is calculated using the equation [8]:

$$E(t) = 1.0183 - 40.6 \times 10^{-6} (t - 20) - 9.5 \times 10^{-7} (t - 20)^2 + 1 \times 10^{-8} (t - 20)^3 \quad (5)$$

where E is the electromotive force, in V, and t is the temperature, in °C.

Weston cell measurement is recommended to be made in the null configuration, where cells are connected back to back and the voltage difference between the two of them is measured. However, this method requires the use of at least 3 cells, among which at least one must be sent to a standardizing laboratory for calibration [8].

If there is no possibility to calibrate the cell, it is recommended that one of them to be used exclusively to calibrate other two, being avoided sudden changes in temperature [7]. Generally, the temperature limits allowed are between 4°C and 40°C [9]. In order to protect the cells by minimizing the risk of high current leakage, one may use protective resistances [9].

Apart from Weston cells the technological evolution has brought on the market other devices, such as the Zener diodes [10,11] or Josephson Junction Array [12], but the equipment that measures and tunes up their reference voltage values has also to be calibrated in a standardised laboratory using the Weston cells. The negative aspect related to the Weston cells is connected to the environmental issues, both mercury and cadmium being toxic heavy metals, but as long as the content of the Weston cell is properly disposed off and sent for recycling, these concerns are fully addressed [7].

2. Results and discussion

The experiments were performed using an H type Weston cell (having internal resistance, r), produced in 1956 by the Institute of Metrology, Romania. It was connected to a voltmeter Voltcraft 4095 (Germany) and an ammeter Kewtech KT 115 (Japan) as a series circuit along with a calibrated resistor box of various resistance values, Voltcraft R-BOX 01 (Germany). The electrical circuit used is presented in Fig. 2.

The ambient temperature was monitored with a thermometer TM 6801B (China), and the recorded value was constant, namely 26.2 °C.

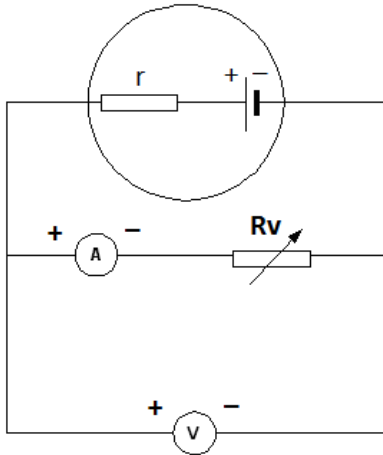


Fig. 2. Experimental layout used for the evaluation of Weston cell

One has varied the external resistance R_v and monitored the current and voltage. Table 1 shows the values of the above mentioned parameters variations.

By plotting the measured values for the cell voltage (resulting from the variation of the external resistance) versus the drawn current, and applying a linear regression procedure (Fig. 3), it was possible to determine the value of the electromotive force (the intercept, $E = 1.0178 \text{ V}$), and the internal resistance (the slope, $r = 2996 \Omega$) at 26.2°C .

Table 1

Current and voltage measured values			
Measurement	R_v, Ω	$I, \mu\text{A}$	U_b, V
1	$2 \cdot 10^6$	0.4	1.014
2	$1 \cdot 10^6$	0.9	1.013
3	$8 \cdot 10^5$	1.2	1.012
4	$6 \cdot 10^5$	1.6	1.011
5	$4 \cdot 10^5$	2.5	1.009
6	$2 \cdot 10^5$	5.0	1.003
7	$1 \cdot 10^5$	9.9	0.990
8	$8 \cdot 10^4$	12.2	0.983
9	$6 \cdot 10^4$	16.1	0.971
10	$4 \cdot 10^4$	23.7	0.950
11	$2 \cdot 10^4$	44.3	0.887
12	$1 \cdot 10^4$	78.3	0.788
13	$8 \cdot 10^3$	92.1	0.742
14	$6 \cdot 10^3$	111.6	0.678

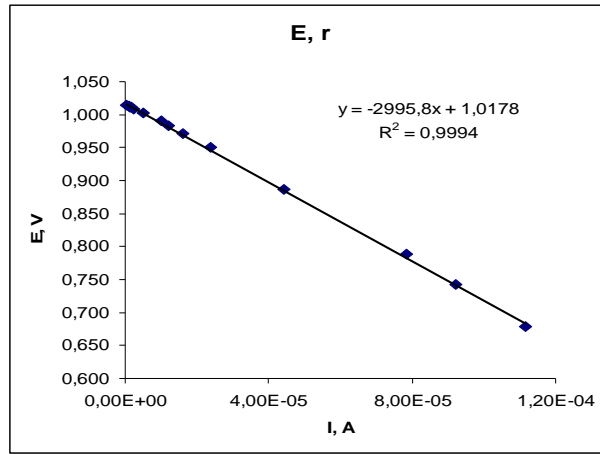


Fig 3. Electromotive force (taken as the intercept) and the voltage variation of Weston cell versus the drawn current

Subsequently, one is now able to determine the Weston cell voltage drift for the considered existence period of 55 years and its corresponding annual value:

$$V_{\text{drift}_{55}} = 1.018104 - 1.0178 = 0.000304 \text{ V} \quad (6)$$

$$V_{\text{drift/year}} = \frac{0.000304}{55} = 5.527 \cdot 10^{-6} \text{ V/year} \quad (7)$$

Taking into account that the experimental temperature was different than the reference temperature and using the equation (5), one may now determine the predicted theoretical value for the electromotive force at 26.2°C in order to compare it with the experimental value:

$$E_{26.2} = 1.0183 - 40.6 \times 10^{-6} (26.2 - 20) - 9.5 \times 10^{-7} (26.2 - 20)^2 + 1 \times 10^{-8} (26.2 - 20)^3 = 1.01801 \text{ V} \quad (8)$$

In order to determine the variation of the electromotive force versus the ambient temperature, the cell was deposited for 24 hours in the fridge and then removed and the electromotive force recorded versus the cell temperature, measured by an infra red thermometer, IR 360, Voltcraft, Germany and the results were plotted in Fig. 4. The result obtained for a temperature of 25 °C, namely 1.0159V is compared to that supplied by equation (5), 1.0185V, and yields a relative error of 0.25%.

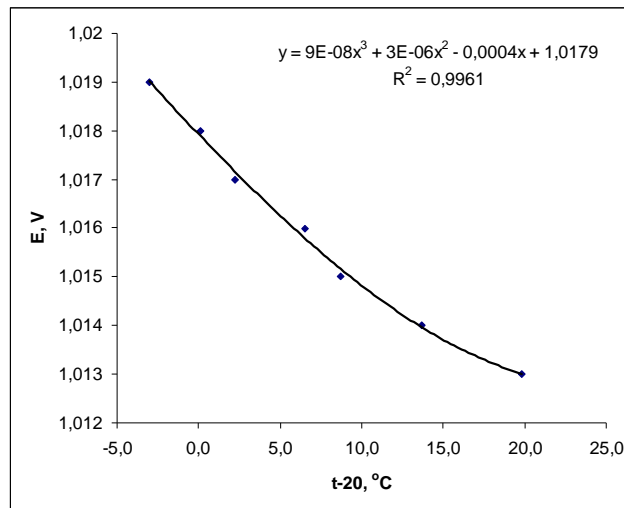


Fig 4. The dependence of the electromotive force on temperature

3. Conclusion

The value of the electromotive force of the investigated Weston cell was found quite stable even after a period of 55 years, $E = 1.0178 \text{ V}$, at 26.2°C , the value of the internal resistance being of the order of thousands ohms ($r = 2996 \Omega$).

The voltage drift was 0.304 mV for the considered period, with an annual voltage drift of $5.527 \mu\text{V/year}$.

Using the recommended equation for the temperature dependence of electromotive force, a relative error of 0.25% in the Weston cell voltage was found.

Based on the above presented results it is expected that the cell will continue to perform adequately if the specific operating conditions and the specification that the drawn current should be limited to 0.1 mA are strictly observed.

REFERENCES

- [1] G. W. Vinal, Comparison of Electrical Standards, Proceedings in Bureau of Standards Journal of Research, **vol. 8**, 1932, pp. 729-748
- [2] P. Vigoureux, S. Watts, The temperature coefficient of the saturated Weston cell, Proceedings of Physical Society, **vol. 45**, no.172, London, 1933
- [3] A. N. Shaw, A Determination of the Electromotive Force of the Weston Normal Cell in Semi-Absolute Volts, Royal Society Publishing, **vol.214**, London, 1913, pp.147-198

- [4] *F. E. Smith*, The Normal Weston Cadmium Cell, R T. Glazebrook, Faraday Royal Society, 1907, pp. 393-421
- [5] *E. Ghali*, Fundamentals of Electrochemical Corrosion, chap. 1, John Wiley & Sons, Inc., New York, 2010, pp 34-36
- [6] *W. J. Hamer*, Standard Cells, Their construction Maintenance and Characteristics, National Bureau of Standards Monograph, **vol. 84**, chap. 5, 1965, pp.15-21
- [7] *C. R. Hoffman*, The Weston Standard Cell, <http://conradhoffman.com/stdcell.htm>
- [8] *K. E. Guthe*, Absolute Electromotive Force of Standard Cells, Bulletin of the Bureau of Standards., **vol. 2** No. 1, 1905, pp. 33-70
- [9] *E. Weston*, Historic Publications in Electrochemistry, United States Patent Office, No. 494,827, Patented, Historic Publications in Electrochemistry, Electrochemical Science and Technology Information Resource (ESTIR), 1893
- [10] *F. K. Harris*, Electrical Measurements, John Wiley & Sons, Inc, New York, chap. 4, 1952, pp. 44-123
- [11] *A. Hastings*, The Art of Analog Layout, 2nd ed., Prentice Hall, 2005
- [12] *J. Kohlmann, R. Behr, T. Funck*, Josephson voltage standards, Meas. Sci. Techn., **vol. 14**, 2003, pp. 1216-1228