

Calculation of the Thermoneutral Potential of NiCd and NiH₂ Cells

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The thermoneutral potential of a nickel cadmium or nickel hydrogen cell is the potential at which the cell charge or discharge process puts out zero heat, and thus is the potential corresponding to the enthalpy change of the charge/discharge reaction, ΔH . A relatively straightforward method for obtaining the thermoneutral potential E_{tn} , is based on the measured potential and temperature derivative of the cell reactions, which are related to the free energy change ΔG , and entropy change ΔS , respectively.

$$\Delta H = \Delta G + T\Delta S \quad (1)$$

$$E_{tn} = E - T \left(\frac{\partial E}{\partial T} \right) \quad (2)$$

Where E is the cell potential, and T is the Kelvin temperature.

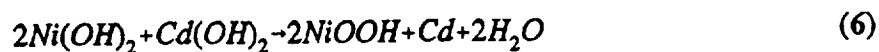
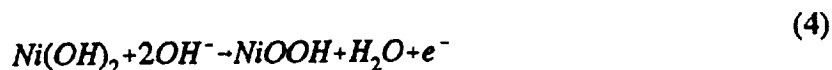
However, since Eq. (2) is derived for a constant pressure system, it does not fully describe the thermoneutral voltage of NiCd and NiH₂ cells, which are constant volume systems in which the pressure can change significantly. Particularly in the nickel hydrogen cell, the pressure of hydrogen can often vary over an order of magnitude or more during the course of a charge or discharge. In a nickel cadmium cell, although significant changes in oxygen pressure can occur during charge or discharge, since oxygen does not enter into the charge/discharge reaction, these pressure changes are related to the heat generated from oxygen evolution and recombination. However, the entropy changes due to changes in hydrogen pressure relative to the 1 atm standard state must be included in Eq. (1) to apply this method to the nickel hydrogen cell. This gives Eq. (3), assuming that the variation in reversible potential with temperature is measured at constant pressure.

In Eq. (3) F is the Faraday constant, and P is the hydrogen pressure in the cell in atm.

$$E_{th} = E - T \left(\frac{\partial E}{\partial T} \right) + \frac{RT \ln P}{2F} \quad (3)$$

Nickel Cadmium Cell

The half reactions, and cell reaction in the nickel cadmium cell are given in Eq. (4)-(6).



The standard potential for reaction (6) is 1.299 volts (Ref. 1). The derivative of voltage with respect to temperature at constant pressure is -0.001514, -0.001014, and -0.0005 volts/K for reactions (4)-(6) respectively (Ref. 2). The value for reaction (4) was derived from the values published in Ref. (2) for the NiCd cell and the cadmium electrode, which are more reliably known than that for the nickel electrode. Thus the value used here for the nickel electrode also includes the effect of approximately a 5% cobalt additive level present in the active material of the NiCd cells.

The thermoneutral potential may be derived from Eq. (2), employing Nernstian expressions for the dependence of potential on reagent concentrations, giving Eq. (7).

$$E_m = \Delta E^\circ - T \left(\frac{\partial \Delta E^\circ}{\partial T} \right) + \frac{RT^2}{F} \left(\frac{\partial \ln[H_2O][NiOOH]}{\partial T} \right) \quad (7)$$

The last term in Eq. (7) is a second order term that is quite small (approximately 10 μ V at 25 deg C). In evaluating the thermoneutral potential of the NiCd cell from Eq. (7), it is found that, to first order, the temperature dependence of the reversible potential cancels out the temperature dependence introduced by the entropic term. Using the reversible potentials and their temperature derivatives for reactions (4)-(6), the thermoneutral potential is found to be 1.448 volts. This voltage is independent of temperature to first

order for the NiCd cell.

Measurements of the thermoneutral potential based on calorimetry have indicated a value of 1.45 volts (Ref. 3). More accurate measurements at different temperatures have indicated 1.454 ± 0.013 volts at 5 deg C, and 1.453 ± 0.004 volts at 20 deg C using data from Ref. 4. All these measurements are in excellent agreement with the value calculated above based on reversible potentials and their temperature coefficients. The temperature derivative of the potential for the nickel electrode reaction may be refined from these data to give -0.001534 volts/K, a value that will be used in the next section for nickel hydrogen cell calculations. These measurements are summarized in Table 1, and are based on measured heat production during discharge over a range of depths-of-discharge, currents, and temperatures. Thermal output was determined by integrating over the charge and discharge cycles, with heat being determined by the difference in temperature between the top and the baseplate of a 50 Ah NiCd battery. The temperature difference was calibrated by holding the battery in steady-state overcharge, where a precisely known thermal output is obtained.

Table 1. Thermal Data for Obtaining Thermoneutral Potentials for NiCd Cells

Test Number	Temp. deg C	DOD	Voltage (volts)	Current (amps)	Power (watts)	Heat (watts)	E_{th} (volts)
1	20	0.167	27.77	14.00	388.85	59.5	1.456
1	20	0.343	27.59	13.77	379.86	59.5	1.450
1	20	0.481	27.53	13.62	374.88	60.0	1.451
2	5	0.302	27.42	20.78	569.76	92.5	1.449
3	20	0.282	27.09	30.76	833.36	154.0	1.459
4	5	0.130	28.36	13.72	389.03	57.0	1.478
4	5	0.270	27.61	13.75	379.72	56.0	1.440
4	5	0.424	27.59	13.59	374.91	58.0	1.448
5	20	0.331	27.26	21.08	574.71	97.5	1.449
6	20	0.357	26.96	30.09	811.15	148.0	1.449
7	20	0.351	27.36	20.83	569.98	99.0	1.460

Table 1A. Average Thermoneutral Potentials for NiCd Cells

	Average E_{th} (volts)	Standard Deviation
5 deg C	1.454	0.013
20 deg C	1.453	0.004
All tests	1.454	0.010

Best Value is 1.454 ± 0.010 volts

Nickel Hydrogen Cell

In the nickel hydrogen cell the reaction at the nickel electrode is nominally the same as that in the NiCd cell, and is given by Eq. (4). The negative electrode reaction and the overall cell reaction are given by Eqs. (8) and (9), respectively.



As can be seen from reaction (9), there is no net change in water or hydroxide as a result of this reaction. The standard reversible potential of reaction (8) is -0.828 volts, and with a temperature coefficient at constant pressure of -0.000834 V/deg. The standard reversible potential of the cell reaction (9) is 1.318 volts. Based on the value for the temperature coefficient of the reversible potential of the nickel electrode calculated for the nickel electrode, the temperature coefficient of the standard potential of the nickel hydrogen cell, i.e. reaction (9), is -0.000700 volts/deg.

Based on Eq. (3) and the Nernst Equation, the thermoneutral potential of the nickel hydrogen cell may be expressed as

$$E_m = \Delta E^\circ - T \left(\frac{\partial E^\circ}{\partial T} \right) - \frac{RT \ln P}{2F} + \frac{RT}{2F} + \frac{RT^2}{F} \left(\frac{\partial \ln[NiOOH]}{\partial T} \right) \quad (10)$$

The first term in Eq. (10) results from the reversible cell potential and the remaining terms from the change in entropy from the electrochemical process, the entropic decrease from hydrogen compression in the cell volume, and the Nernst Eq. These terms are arranged in decreasing order of significance. At 25 deg C the first term is 1.318 V, the second term is 0.2086 volts, the third term is -0.0295 volts at 10 atm of hydrogen, the fourth term is 0.0128 volts, and the last term is negligible. Thus at 25 deg C the thermoneutral potential of a nickel hydrogen cell is $1.5394 - 0.01284 \ln P$ volts. At 0 deg C it is $1.5384 - 0.01284 \ln P$ volts. These values are approximately 30 mv lower than those in Ref. 5. This difference may in part be due to the use of potentials and temperature derivatives here based on nickel electrodes containing approximately 5% cobalt additive. This additive is known to decrease the reversible potential of the nickel electrode by about 30-40 mV.

Conclusions

The thermoneutral voltage of the nickel hydrogen cell has been semi-empirically evaluated based on the best available thermal data for the nickel cadmium cell, and the known thermodynamics of the cadmium and hydrogen electrodes. The thermoneutral potential thus obtained is dependent on both hydrogen pressure and cell temperature. At room temperature and average cell pressures of about 300 psia, the thermoneutral potential thus obtained is 1.501 volts, which is in reasonable agreement with the value of 1.51 volts commonly employed. In utilizing this voltage for thermal calculations it is necessary to also include heat from self-discharge and oxygen recombination as additional, and independent terms.

References

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