THERMODYNAMICS OF NICKEL-CADMIUM AND NICKEL-HYDROGEN BATTERIES

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ABSTRACT

Thermodynamic parameters for Nickel-Cadmium (NiCad) and Nickel-Hydrogen (NiH$_2$) batteries are calculated for temperatures ranging from 273.15K (0°C) to 373.15K (100°C). For both systems, we list equilibrium and thermoneutral voltages for the cells, and in the case of the NiH$_2$ battery, these data are provide for hydrogen fugacities ranging from 0.01 to 100 (atm) to simulate the full discharged and charged states. The quality of the input thermodynamic data are assessed and the effect of assuming different cell reactions is analyzed.

INTRODUCTION

Nickel-cadmium (NiCad) and nickel-hydrogen (NiH$_2$) batteries are used extensively in aerospace systems, because of their relatively high energy and power densities and their excellent cycling capabilities [1-4]. However, given the severe demands placed on cycling performance for satellites in low earth orbit (LEO) and recognizing the need to keep battery weight to an absolute minimum, efforts continue to improve the cycle life particularly to high depths of discharge. The current standard in this regard for NiH$_2$ batteries is a cycle life of 30,000 cycles to 50% loss in capacity (of the nickel electrode) at 50% depth of discharge. The cycle life of NiCad batteries is not as favorable (generally a few thousand cycles), so that these systems are commonly not employed where cycle life is the key operational characteristic.

It is well recognized that the cycle lives of NiCad and NiH$_2$ batteries are limited by irreversible structural and physicochemical changes that occur in the porous nickel electrodes as the batteries are cycled between the charged and discharged states. Although the mechanistic details of the degradation processes are not well-understood, various models have been developed that provide a good phenomenological simulation of the loss of capacity [5,6]. However, a complete understanding of the degradation mechanisms requires a careful analysis of the cell thermodynamics so that the voltage and energy efficiencies can be placed on a rational basis. Thermodynamic data for a variety of alkaline batteries has been published previously by Pound, Singh, and Macdonald [7] and for sealed NiCad batteries by Hodge et al [8]. The present work recalculates and expands the thermodynamic database for the

NiCad and NiH$_2$ systems by deriving values for relevant parameters (equilibrium cell and thermoneutral potentials) over a wide range of temperature (0°C – 100°C) and, in the case of NiH$_2$, hydrogen pressure (0.01 – 100 atm).
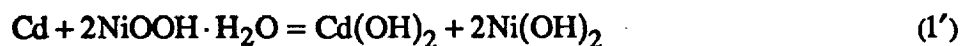
BATTERY THERMODYNAMICS

Following conventional formalism, the cell reactions for NiCad and NiH$_2$ batteries can be written as
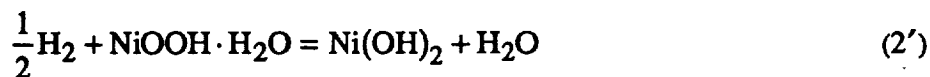
$$Cd + 2\ NiOOH + 2H_2O = Cd(OH)_2 + 2Ni(OH)_2 \qquad (1)$$

and

$$\frac{1}{2}H_2 + NiOOH = Ni(OH)_2 \qquad (2)$$

respectively, assuming that the charged nickel active material is NiOOH, or as

$$Cd + 2NiOOH \cdot H_2O = Cd(OH)_2 + 2Ni(OH)_2 \qquad (1')$$

and

$$\frac{1}{2}H_2 + NiOOH \cdot H_2O = Ni(OH)_2 + H_2O \qquad (2')$$

if NiOOH $\cdot$ H$_2$O is assumed to be the active material at the nickel positive electrode [8]. The equilibrium voltages for these four reactions are given by the Nernst equation as

$$\Delta E_{cell}^e = \Delta E_{cell}^o + \frac{2.303RT}{F}\ \log a_{H_2O} \qquad (3)$$

$$\Delta E_{cell}^e = \Delta E_{cell}^o + \frac{2.303RT}{F}\ \log f_{H_2}^{1/2} \qquad (4)$$

$$\Delta E_{cell}^e = \Delta E_{cell}^o \qquad (3')$$

and

$$\Delta E_{cell}^e = \Delta E_{cell}^o + \frac{2.303RT}{F}\ \log f_{H_2}^{1/2} - \frac{2.303RT}{F}\log a_{H_2O} \qquad (4')$$

where f_{H_2} is the fugacity of hydrogen, a_{H_2O} is the activity of water, and the standard cell voltages are given by

$$\Delta E_{cell}^o = -\Delta G_{cell}^o\ /\ nF \qquad (5)$$

ΔG^0_{cell}, n, and F are the change in standard Gibbs energy for the cell, the number of electrons involved in the cell reaction, and Faraday's constant, respectively. The change in standard Gibbs energy for the cell is

$$\Delta G^0_{cell} = \sum_{Products} v_P \Delta_f G^0_P - \sum_{Reactants} v_R \Delta_f G^0_R \tag{6}$$

where $\Delta_f G^0_I$ is the standard Gibbs energy of formation of component I, n is the stoichiometric coefficient for the reaction, and subscripts P and R refer to "products" and "reactants," respectively, in the cell reactions (i.e. Reactions (1), (2), (1'), and (2')).

A full assessment of the thermodynamics of a battery requires the estimation of the thermoneutral potential of the cell, defined as

$$\Delta E^T_{cell} = -\Delta H_{cell} / nF \tag{7}$$

and hence

$$\Delta E^T_{cell} = \Delta E^e_{cell} - T \left(\frac{\partial \Delta E^e_{cell}}{\partial T} \right) \tag{8}$$

Using standard thermodynamic identities, we derive expressions for ΔE^T_{cell} for the four cells of interest as

$$\Delta E^T_{cell,1} = - \frac{\Delta H^0_1}{2F} - \frac{RT^2}{F} \left[\frac{\partial \ln a_{H_2O}}{\partial T} \right] \tag{9}$$

$$\Delta E^T_{cell,2} = - \frac{\Delta H^0_2}{F} \tag{10}$$

$$\Delta E^T_{cell,1'} = - \frac{\Delta H^0_{1'}}{2F} \tag{11}$$

and

$$\Delta E^T_{cell,2'} = - \frac{\Delta H^0_{2'}}{F} + \frac{RT^2}{F} \left[\frac{\partial \ln a_{H_2O}}{\partial T} \right] \tag{12}$$

where ΔH^0_k is the change in standard enthalpy for Reaction k. Note that a term involving the fugacity of hydrogen does not appear in Equations (10) and (11) [corresponding to Reactions (2) and (2')], because we have assumed that f_{H_2} is a constant, independent of temperature.

THERMODYNAMIC DATA

The thermodynamic data employed in this study are summarized in Tables 1 and 2, together with the sources from which they were taken. Heat capacities for $Ni(OH)_2$, $Cd(OH)_2$, $NiOOH \cdot H_2O$, and $NiOOH$ had to be estimated using C_p^o/S^o ratios, which are found to be constant for given classes of compounds [7]. The value adopted for the Gibbs energy of formation for $Cd(OH)_2$ was adjusted slightly from that given by Naumov et al (Ref. (a), Table 1), 474.5 kJ/mol, so as to yield the observed equilibrium voltage for the NiCad battery [1.45V (2)]. The accuracies of the various thermodynamic quantities summarized in Table 1 are largely unknown and are difficult to estimate without detailed information on the original experiments from which they are derived.

Noting that heat capacities are generally expressed in the form

$$C_p^o = A + BT + CT^{-2} \tag{13}$$

we derived expressions for the Gibbs energy and enthalpy of formation of any given compound at temperature T as follows.

$$\Delta_f G_T^o = \Delta_f G_{T_0}^o - (T - T_0)\Delta_f S_{T_0}^o + A_f\left[T - T_0 - T\ln\left(\frac{T}{T_0}\right)\right]$$

$$+ B_f\left[\frac{T^2 - T_0^2}{2} - T(T - T_0)\right] + C_f\left[\frac{1}{T} - \frac{1}{T_0}\right]\left[\frac{T}{2}\left(\frac{1}{T} + \frac{1}{T_0}\right) - 1\right] \tag{14}$$

$$\Delta_f H_T^o = \Delta_f H_{T_0}^o + A_f(T - T_0) + \frac{B_f}{2}\left[T^2 - T_0^2\right] - C\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{15}$$

and

$$\Delta_f S_T^o = \left(\Delta_f H_T^o - \Delta_f G_T^o\right)/T \tag{16}$$

where $\Delta_f S_{T_0}^o$ and $\Delta_f H_{T_0}^o$ are the entropy and enthalpy of formation at the reference temperature ($T_0 = 298.15K$) and A_f, B_f, and C_f are the coefficients in Equation (13) for the formation of the compound of interest.

Thermodynamic parameters of formation calculated using Equations (14) to (16) for various active components in NiCad and NiH_2 batteries are summarized in Table 3 as a function of temperature from 273.15K (0°C) to 373.15K

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(100°C). Note that no values are given for Cd and H_2 because, by definition, the parameters of formation are zero at all temperatures.

Calculation of the equilibrium and thermoneutral cell voltages requires a knowledge of the activity of water, which for 8 molal KOH can be expressed as (7)

$$\ln a_{H_2O} = -6.345750 + 6.125771 \times 10^3 / T - 2.093874 \times 10^6 / T^2$$

(17)

$$+2.324516 \times 10^8 / T^3$$

The activity of water for this electrolyte ranges from 0.514 at 263.15K to 0.618 at 393.15K.

The data summarized in Table 3 were used to estimate equilibrium and thermoneutral cell voltages for NiCad and NiH_2 batteries as a function of temperature, as given in Tables 4-7. We should note, at this point, that the thermodynamic data for $NiOOH \cdot H_2O$ are poorly known, so that lower confidence should be placed in the potentials calculated from Reactions (1') and (2') than is those calculated from Reactions (1) and (2). Accordingly, in this work, we will emphasize the thermodynamic calculations that involve NiOOH as the oxidized, active material at the positive electrodes of NiCad and NiH_2 batteries.

DISCUSSION

As seen from the data summarized in Tables 4 and 5, the equilibrium potentials for NiCad and NiH_2 batteries with 8m KOH electrolyte decrease with increasing temperature and, for the latter system at any given temperature, increase with increasing hydrogen partial pressure. The dependence of ΔE_{cell}^e on temperature results directly from the entropy and heat capacity changes for the cell reactions as well as from the change in water activity in the electrolyte, whereas the dependence on hydrogen pressure (in the case of NiH_2 batteries) results directly from the thermodynamics of the negative electrode. We also note that much larger changes in ΔE_{cell}^e with temperature are predicted if the oxidized nickel phase is assumed to be $NiOOH \cdot H_2O$ rather than NiOOH, but the poor quality of the data for the former precludes any in-depth analysis of this difference.

Thermoneutral potentials for NiCad and NiH_2 batteries are listed in Tables 6 and 7. The thermoneutral voltage corresponds to that voltage that the cell would have to operate at so that the entropic dissipation of energy is zero. Of course, the data calculated in this work do not include the various irreversible sources of energy dissipation, associated with heat generation due to the internal cell resistance and arising from the reactions occurring at the

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electrodes on charging and discharging. These irreversible effects are best treated using irreversible thermodynamic methods of the type proposed by Ratjke et al [9].

For both the NiCad and NiH$_2$ batteries, the thermoneutral voltage is greater than the equilibrium cell voltage at equivalent temperatures and hydrogen pressure (for the NiH$_2$ system). This relationship arises from the fact that the entropy changes for the cell reactions on discharge are negative, corresponding to exothermic processes. Likewise, on charging both cells are endothermic provided that the voltage lies between ΔE_{cell}^e and ΔE_{cell}^T.

Finally, we note that the equilibrium cell potentials calculated in this work for the NiH$_2$ battery are in good agreement with our previous calculations and with experimental data [7]. A similar comparison cannot be made with experimental data for NiCad batteries because we have used these data to adjust the Gibbs energy of formation of Cd(OH)$_2$ used in the calculations. However, it is worth noting that our equilibrium cell potential at 25°C (1.45V) is significantly more positive than that calculated by Hodge et al [8] (1.29V). This difference may be attributed to the large uncertainty in the Gibbs energy of formation for NiOOH · H$_2$O [8] and to the fact that Hodge et al [8] did not apply a correction for the activity of water. Clearly, the calculated value of Hodge et al [8] is much lower than the open circuit voltage of 1.45V quoted by Halpert [2]. Because irreversible processes within the cell are expected to reduce the measured open circuit voltage below the equilibrium cell voltage, it is evident that the calculations of Hodge et al (8) are at odds with experiment.

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TABLE 1

Thermodynamic Properties of Components at 298.15K

Component	$\Delta_f G^o$ (kJ/mol)		$\Delta_f H^o$ (kJ/mol)		$\Delta_f S^o$ (f) (J/K.mol)	S^o (J/K.mol)		$\Delta_f C_p^o$ (a,b,f) (kJ/mol)
Ni	0		0		0	29.87	(f)	$16.987 + 0.02946T$
Cd	0		0		0	51.756	(a)	$22.217 + 0.012301T$
O_2	0		0		0	205.03	(f)	$29.957 + 0.00414T - 1.674 \times 10^5 \, T^{-2}$
H_2	0		0		0	130.574	(a)	$27.2797 + 0.0032635T + 0.50208 \times 10^5 \, T^{-2}$
H_2O	-237.178	(a)	-285.828	(d)	-163.174	69.915	(a)	$10.669 + 0.042284T - 6.90308 \times 10^5 T^{-2}$
$Ni(OH)_2$	-459.070	(b)	-541.799	(d)	-277.474	88.0	(f)	$18.106 - 0.03686T + 1.1719 \times 10^{-5} T^{-2}$
NiOOH	-321.7	(b)	-391.231	(d)	-233.207	66.98	(b)	$30.186 - 0.03523T + 1.423 \times 10^5 T^{-2}$
$NiOOH \cdot H_2O$	-564.422	(c)	-629.859	(d)	-219.478	150.624	(c)	$87.388 - 0.082844T + 8.661 \times 10^5 T^{-2}$
$Cd(OH)_2$	-482.347		-571.642	(d)	-299.496	87.864	(a)	$12.726 - 0.0197T + 1.17192 \times 10^5 T^{-2}$

(a) G.B. Naumov, et al, Handbook of Thermodynamic Data, USGS-WRD-74-001, US Geol. Survey, 1974.

(b) P.G. Pound, R.P. Singh, & D.D. Macdonald, J. Power Sources, 18, 1 (1986).

(c) B.J.R. Hodge et al, J. Power Sources, 7, 211 (1975).

(d) Estimated from $\Delta_f H^o = \Delta_f G^o + T\Delta_f S^o$.

(e) Calculated for the formation reaction from the elements.

(f) D.D. Wagman et al, J. Phys. Chem. Ref. Data, 11, Suppl. No. 2 (1982).

TABLE 2

Heat Capacities of Active Compounds (a,b,f, Table 1)

Compound	C_p^o (kJ/mol)
H_2O	$52.928 + 47.614 \times 10^{-3} T - 7.238 \times 10^5 T^{-2}$
$Ni(OH)_2$	92.33
NiOOH	90.77
$NiOOH \cdot H_2O$	200.09
$Cd(OH)_2$	92.18

TABLE 3

Thermodynamic Parameters of Formation for Active Components in NiCad
and NiH$_2$ Batteries as a Function of Temperature

Temperature (K)	Gibbs Energy (J/mol)	Enthalpy (J/mol)	Entropy (J/K-mol)
		Ni(OH)$_2$	
273.15	-466014.9	-541988.4	-278.1382
283.15	-463234.9	-541909.9	-277.8557
293.15	-460457.7	-541835.1	-277.5959
298.15	-459070	-541799	-277.474
303.15	-457682.9	-541763.9	-277.3572
313.15	-454910.5	-541696.4	-277.1382
323.15	-452140.1	-541632.6	-276.9376
333.15	-449371.7	-541572.5	-276.7544
343.15	-446605	-541516.1	-276.5875
353.15	-443839.8	-541463.4	-276.436
363.15	-441076.2	-541414.3	-276.299
373.15	-438313.8	-541368.9	-276.1758
		NiOOH	
273.15	-327593.5	-391776.8	-234.9745
283.15	-325230.3	-391554.5	-234.237
293.15	-322874.9	-391337	-233.5396
298.15	-321700	-391230	-233.205
303.15	-320526.8	-391124.2	-232.8793
313.15	-318185.7	-390915.9	-232.2536
323.15	-315851.2	-390712	-231.66
333.15	-313522.9	-390512.6	-231.0964
343.15	-311200.5	-390317.4	-230.5608
353.15	-308883.8	-390126.4	-230.0517
363.15	-306572.3	-389939.7	-229.5673
373.15	-304266	-389757	-229.1063
		NiOOH·H$_2$O	
273.15	-570232.1	-631718.9	-225.1038
283.15	-567888.4	-630963.5	-222.763
293.15	-565571.2	-630224	-220.5461
298.15	-564422	-629860	-219.481
303.15	-563278.9	-629499.7	-218.4432
313.15	-561010.3	-628789.9	-216.4453
323.15	-558764.1	-628093.9	-214.5448
333.15	-556539.2	-627411.5	-212.7346
343.15	-554334.6	-626742	-211.0085
353.15	-552149.4	-626085.1	-209.3611
363.15	-549982.6	-625440.3	-207.7873
373.15	-547833.4	-624807.5	-206.2827

TABLE 3 (continued)

Temperature (K)	Gibbs Energy (J/mol)	Enthalpy (J/mol)	Entropy (J/K-mol)
		Cd(OH)$_2$	
273.15	-489876.4	-571855.4	-300.1235
283.15	-486862.4	-571767.8	-299.8593
293.15	-483851.4	-571683.2	-299.6129
298.15	-482347	-571642	-299.496
303.15	-480843.3	-571601.5	-299.383
313.15	-477837.8	-571522.6	-299.1684
323.15	-474834.8	-571446.4	-298.9677
333.15	-471834	-571372.9	-298.7802
343.15	-468835.5	-571302.1	-298.6049
353.15	-465839	-571233.7	-298.441
363.15	-462844.4	-571167.9	-298.2878
373.15	-459851.5	-571104.5	-298.1446
		H$_2$O	
273.15	-241078.8	-286186.8	-165.1239
283.15	-239514.8	-286051.7	-164.3391
293.15	-237955.6	-285906.4	-163.5557
298.15	-237178	-285830	-163.165
303.15	-236401.7	-285751.3	-162.7751
313.15	-234852.9	-285587	-161.9981
323.15	-233309.6	-285414	-161.2256
333.15	-231771.8	-285232.7	-160.458
343.15	-230239.5	-285043.4	-159.6957
353.15	-228712.8	-284846.5	-158.939
363.15	-227191.8	-284642.2	-158.188
373.15	-225676.6	-284430.8	-157.4429

TABLE 4

Calculated Equilibrium Cell Voltages for NiCad Batteries as a Function of Temperature

T/K	ΔE^e_{cell} (V)	
	Reaction (1)	Reaction (1')
273.15	1.461	1.459
283.15	1.457	1.438
293.15	1.453	1.418
298.15	1.450	1.408
303.15	1.448	1.397
313.15	1.444	1.377
323.15	1.439	1.356
333.15	1.435	1.334
343.15	1.430	1.313
353.15	1.425	1.292
363.15	1.420	1.270
373.15	1.415	1.248

TABLE 5

Calculated Equilibrium Cell Voltages for NiH_2 Batteries as a Function
of Temperature and Hydrogen Pressure

	pH_2/atm				
T/K	0.01	0.1	1.0	10.0	100.0

Reaction 2

273.15	1.380	1.408	1.435	1.462	1.489
283.15	1.374	1.402	1.430	1.458	1.487
293.15	1.368	1.397	1.426	1.455	1.484
298.15	1.365	1.394	1.424	1.453	1.483
303.15	1.361	1.391	1.422	1.452	1.482
313.15	1.355	1.386	1.417	1.448	1.479
323.15	1.348	1.381	1.413	1.445	1.477
333.15	1.342	1.375	1.408	1.441	1.474
343.15	1.335	1.369	1.403	1.437	1.471
353.15	1.329	1.364	1.399	1.434	1.469
363.15	1.322	1.358	1.394	1.430	1.466
373.15	1.315	1.352	1.389	1.426	1.463

Reaction (2')

273.15	1.459	1.432	1.405	1.378	1.351
283.15	1.440	1.412	1.384	1.356	1.327
293.15	1.420	1.391	1.362	1.333	1.304
298.15	1.410	1.381	1.351	1.322	1.292
303.15	1.401	1.371	1.341	1.311	1.281
313.15	1.382	1.351	1.320	1.289	1.258
323.15	1.362	1.330	1.298	1.266	1.234
333.15	1.342	1.309	1.276	1.243	1.210
343.15	1.322	1.288	1.254	1.220	1.186
353.15	1.302	1.267	1.232	1.197	1.162
363.15	1.282	1.246	1.210	1.174	1.138
373.15	1.262	1.225	1.188	1.151	1.114

TABLE 6

Calculated Thermoneutral Cell Voltages for NiCad Batteries as a
Function of Temperature

	ΔE_{cell}^{T} (V)	
T/K	Reaction (1)	Reaction (1′)
273.15	1.580	2.033
283.15	1.574	2.040
293.15	1.570	2.046
298.15	1.569	2.050
303.15	1.568	2.053
313.15	1.568	2.059
323.15	1.569	2.065
333.15	1.572	2.071
343.15	1.575	2.077
353.15	1.580	2.083
363.15	1.585	2.089
373.15	1.591	2.095

TABLE 7

Calculated Thermoneutral Cell Voltages for NiH_2 Batteries as a Function of
Temperature and Hydrogen Pressure

T/K	0.01	0.1	1.0	10.0	100.0
			pH_2/atm		

Reaction 2

T/K	0.01	0.1	1.0	10.0	100.0
273.15	1.611	1.584	1.557	1.530	1.503
283.15	1.615	1.586	1.558	1.530	1.502
293.15	1.618	1.589	1.560	1.531	1.502
298.15	1.620	1.590	1.561	1.531	1.501
303.15	1.621	1.591	1.561	1.531	1.501
313.15	1.625	1.594	1.563	1.532	1.501
323.15	1.628	1.596	1.564	1.532	1.500
333.15	1.632	1.599	1.566	1.533	1.500
343.15	1.635	1.601	1.567	1.533	1.499
353.15	1.639	1.604	1.569	1.533	1.498
363.15	1.642	1.606	1.570	1.534	1.498
373.15	1.645	1.608	1.571	1.534	1.497

Reaction (2′)

T/K	0.01	0.1	1.0	10.0	100.0
273.15	2.065	2.038	2.011	1.983	1.956
283.15	2.081	2.053	2.025	1.997	1.969
293.15	2.094	2.065	2.036	2.007	1.978
298.15	2.100	2.071	2.041	2.012	1.982
303.15	2.106	2.076	2.046	2.016	1.986
313.15	2.116	2.085	2.054	2.023	1.992
323.15	2.124	2.092	2.060	2.028	1.996
333.15	2.131	2.098	2.065	2.032	1.999
343.15	2.137	2.103	2.069	2.035	2.001
353.15	2.142	2.107	2.072	2.037	2.002
363.15	2.156	2.110	2.074	2.038	2.002
373.15	2.149	2.112	2.075	2.038	2.001