Supplementary Information for

Improved Electrochemical Phase Diagrams from Theory and Experiment: The Ni-Water System and its Complex Compounds

Liang-Feng Huang[1], M. J. Hutchison[2], R. J. Santucci Jr.[2], John R. Scully[2], and James M. Rondinelli[1]*

1. Department of Materials Science & Engineering, Northwestern University, Evanston, IL 60208, USA

2. Department of Materials Science & Engineering, University of Virginia, Charlottesville, VA 22904, USA

*Corresponding Author: jrondinelli@northwestern.edu

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(A) Structural Information

(i) Lattice constants and angles of unit cells

The units for lattice constants and angles are angstrom and degree, respectively.

	Space Group	Formula Units	HSE06	PBEsol
Ni	*Fm*-3*m* #225	1	*a*/*b*/*c* = 2.475 α/β/γ = 60.0	2.448 60.0
NiO	*R*-3*m* #166	2	*a*/*c* = 2.951 *b* = 5.093 α = 106.84 β = 120.27 γ = 73.17	2.920 5.006 106.96 120.00 73.04
Ni_3O_4	*Fd*-3*m* #227	8	*a* = 8.256 *b* = 8.093 *c* = 8.036 α/β/γ = 90.0	8.015 8.015 8.015 90.0
Ni_2O_3	*R*-3*c* #167	2	*a*/*b*/*c* = 5.166 α/β/γ = 56.3	5.165 55.49
NiO_2	*P*-3*m*1 #164	1	*a*/*b* = 2.753 *c* = 4.636 α/β = 90.0 γ = 120.0	2.783 4.665 90.0 120.0
$Ni(OH)_2$	*P*-3*m*1 #164	1	*a*/*b* = 3.129 *c* = 4.587 α/β = 90.0 γ = 120.0	3.115 4.395 90.0 120.0
NiOOH	*R*-3*m* #166	2	*a*/*b* = 2.909 *c* = 9.705 α = 90.0 β = 72.2 γ = 120.0	2.913 9.424 90.0 72.0 120.0

(ii) Atomic fractional coordinates in unit cells

NiO, Space Group *R*-3*m* #166, 2 Ni atoms and 2 O atoms

0.000083	0.000041	0.000014
0.500083	0.500040	0.500014
0.249916	0.249958	0.749985
0.749916	0.749959	0.249985

Ni_3O_4, Space Group *Fd*-3*m* #227, 24 Ni atoms and 32 O atoms

0.125055	0.126988	0.123796
0.877483	0.874844	0.875766
0.623669	0.124845	0.624464
0.374957	0.873347	0.376587
0.122525	0.626373	0.623646
0.877369	0.373996	0.374863
0.622939	0.625536	0.125375
0.376209	0.373644	0.875713
0.500347	0.499869	0.499871
0.249681	0.749983	-0.000094
0.750457	0.248565	0.001197
0.750448	0.000363	0.249865
0.249474	-0.000359	0.749636
-0.000238	0.249928	0.749977
0.001392	0.750113	0.249972
0.498661	-0.000017	0.000574
0.249596	0.250278	0.500119
0.750444	0.751217	0.498769
0.750456	0.500091	0.749379
0.249523	0.499754	0.251119
0.000276	0.499836	0.000204
0.498693	0.249651	0.250248
0.499921	0.750215	0.749891
0.000740	0.000441	0.499396
0.255430	0.262649	0.257493
0.743599	0.750287	0.737768
0.492414	0.992005	0.757949
0.500700	0.008630	0.242086
0.988498	0.759095	0.494583
0.006334	0.241479	0.507007
0.758333	0.490687	-0.001105
0.242471	0.505451	0.009800
0.010543	0.505775	0.244735
0.991767	0.492123	0.754990
0.506001	0.243118	0.006577
0.491891	0.756213	0.994904
0.244463	0.005500	0.509372
0.755597	0.994391	0.486641
0.255947	0.757853	0.754432
0.744092	0.238431	0.241188
0.490342	0.492158	0.259206
0.507336	0.507765	0.740885
0.994105	0.256746	0.991902
0.008191	0.743783	0.005720
0.007318	0.008361	0.742288
0.999754	0.993210	0.257785
0.511139	0.741206	0.504976
0.493646	0.258574	0.494431
0.758437	0.249970	0.761480
0.244569	0.736742	0.246111
0.255484	0.494816	0.490655
0.744147	0.508496	0.501337
0.744190	0.006857	0.012721
0.255474	0.993948	0.990244
0.756214	0.761555	0.258787
0.241470	0.242597	0.742694

Ni_2O_3, Space Group *R*-3*c* #167, 4 Ni atoms and 6 O atoms

0.149841	0.149717	0.149799
0.349994	0.350111	0.350130
0.653787	0.653636	0.653707
0.846410	0.846330	0.846383
0.467660	0.749898	0.032440
0.924920	0.575171	0.250080
0.749831	0.032653	0.467728
0.250231	0.924733	0.574937
0.032403	0.467590	0.749963
0.574919	0.250155	0.924829

NiO_2, Space Group *P*-3*m*1 #164, 1 Ni atoms and 2 O atoms

-0.000000	0.000000	-0.000000
0.333329	0.666671	0.201445
0.666670	0.333328	0.798554

$Ni(OH)_2$, Space Group *P*-3*m*1 #164, 1 Ni atoms, 2 O atoms, and 2 H atoms

-0.000000	-0.000000	0.000003
0.333328	0.666671	0.219711
0.666671	0.333328	0.780265
0.333334	0.666665	0.429149
0.666665	0.333334	0.570870

NiOOH, Space Group *R*-3*m* #166, 2 Ni atoms, 4 O atoms, and 2 H atoms

0.075944	0.055883	0.003747
0.076417	0.055714	0.503747
0.274865	0.654760	0.104882
0.261099	0.647462	0.615431
0.891729	0.463971	0.392061
0.877041	0.457003	0.902607
0.037048	0.538347	0.282211
0.115539	0.573176	0.725280

(iii) Supercells used in phonon calculations

Material	**Supercell**
Ni	2×2×2
NiO	2×2×2
Ni_3O_4	2×2×2
Ni_2O_3	2×2×2
NiO_2	4×4×2
$Ni(OH)_2$	4×4×2
NiOOH	2×2×2

In addition, the vibrational frequencies of O_2 and H_2 molecules are calculated in a large vacuum-periodic supercell (15×15×15 $Å^3$), which fully isolates these molecules from their periodic images.

(B) Thermodynamic Energies

The total free energy of a solid/gas is expressed as

$G_{tot}(T) = \varepsilon + G_T$,

Where ε and G_T are the total electronic energy and the temperature-dependent contributions, respectively. G_T includes the contributions from the electronic excitation (in metal, e.g., Ni), atomic vibrations, and molecular rotation and translation (in O_2 and H_2 gases). The G_T's for the standard O_2 and H_2 gases (298.15 K, 1.0 bar) are derived by summing their calculated zero-point energies (ZPEs) and measured G_T drops from 0 to 298.15 K **[1]**.

The reaction equation between a Ni compound ($Ni_xO_yH_z$) and the references (i.e., Ni, O_2, and H_2) can be written as

$$Ni_xO_yH_z = xNi + \frac{y}{2}O_2 + \frac{z}{2}H_2 .$$

Then, its free energy of formation ($\Delta_f G$) can be calculated using

$$\Delta_f G = G_{tot}(Ni_xO_yH_z) - \left\{ xG_{tot}(Ni) + \frac{y}{2}G_{tot}(O_2) + \frac{z}{2}G_{tot}(H_2) \right\} = \Delta_f \varepsilon + \Delta G_T ,$$

Where,

$$\Delta_f \varepsilon = \varepsilon(Ni_xO_yH_z) - \left\{ x\varepsilon(Ni) + \frac{y}{2}\varepsilon(O_2) + \frac{z}{2}\varepsilon(H_2) \right\}$$

is the electronic energy of formation, and

$$\Delta G_T = G_T(Ni_xO_yH_z) - \left\{ xG_T(Ni) + \frac{y}{2}G_T(O_2) + \frac{z}{2}G_T(H_2) \right\}$$

is the thermal correction.

The calculated zero-point energy (ZPE) and G_T and ΔG_T at 298.15 K for all the considered species are listed below:

Species	ZPE (eV)	G_T (eV)	ΔG_T (eV)
Ni	0.040	0.002	0.000
O_2	0.099	-0.445	0.000
H_2	0.265	-0.051	0.000
NiO	0.105	0.050	0.275
Ni_3O_4	0.469	0.315	1.211
Ni_2O_3	0.359	0.266	0.940
NiO_2	0.258	0.210	0.657
$Ni(OH)_2$	0.801	0.715	1.213
NiOOH	0.466	0.349	0.818

For solids, the standard chemical potential (μ^s) equals $\Delta_f G$, i.e., $\mu^s = \Delta_f G$.

For aqueous ions, the concentration-dependent chemical potential (μ^I) is calculated using

$\mu^I = \mu_0^I + RT\ln([I])$,

where, R is the gas constant (8.314 J-mol^{-1}K^{-1}); μ_0^I is the chemical potential of ion I at the standard condition (298.15 K, 1.0

bar, 1.0 mol/L, and pH=0) obtained from various experimental databases; [*I*] is the aqueous-ion activity, and approximated to be the concentration of ion *I*. For H^+ ion, its μ_0 at the standard condition (298.15 K, pH 0, 1.0 bar) equals 0, therefore, it μ can be expressed as

$$\mu = RT\ln([H^+]) = -RT\ln(10) \bullet p\mathrm{H}.$$

The μ_0^I's (in eV/f.u.) of the considered Ni aqueous ions, as well as μ^S's (in eV/f.u.) of Ni compounds, from the databases by Pourbaix [2], Burgess [3], Bard [4], and Beverskog [5] are listed below.

Species	Pourbaix	Burgess	Bard	Beverskog
Ni^{2+}	-0.500	-0.456	-0.481	-0.478
Ni^{3+}	—	+3.745	—	—
$NiOH^+$	—	—	—	-2.355
$Ni(OH)_3^-$	-6.077	—	—	-6.079
$Ni(OH)_4^{2-}$	—	—	—	-7.708
NiO	—	—	—	-2.188
Ni_3O_4	-7.379	—	—	—
Ni_2O_3	-4.869	—	—	—
NiO_2	-2.230	—	—	-2.005
$Ni(OH)_2$	-4.696	—	-4.696	-4.756
NiOOH	—	—	—	-3.406

(C) Reaction Paths and Chemical Potentials of Reaction

The reaction paths that connect all the considered species, as well as the corresponding chemical potentials of reaction ($\Delta\mu$, in J/mol) are listed below, where F ($= eN_A = 9.65\times10^4\,\mathrm{C}\bullet\mathrm{mol}^{-1}$) is the Faraday constant. In our calculations of $\Delta\mu$'s, Ni^{2+} is used as the electrochemical reference, thus, it always resides at the right parts of the reaction paths designed here.

The chemical potentials of solids and aqueous ions as described in previous section are used here to calculate $\Delta\mu$'s, and it should be noted that the chemical potentials for aqueous ions are concentration dependent.

(1) $\mathrm{Ni} \rightarrow \mathrm{Ni}^{2+} + 2e^-$

$$\Delta\mu\left(\mathrm{Ni}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{Ni}\right) - \mu\left(\mathrm{Ni}^{2+}\right) + 2F\bullet E_{\mathrm{SHE}} = -\mu\left(\mathrm{Ni}^{2+}\right) + 2F\bullet E_{\mathrm{SHE}}$$

(2) $\mathrm{Ni}^{3+} + e^- \rightarrow \mathrm{Ni}^{2+}$

$$\Delta\mu\left(\mathrm{Ni}^{3+}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{Ni}^{3+}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - F\bullet E_{\mathrm{SHE}}$$

(3) $\mathrm{NiOH}^{+} + \mathrm{H}^{+} \rightarrow \mathrm{Ni}^{2+} + \mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{NiOH}^{+}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{NiOH}^{+}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - \mu\left(\mathrm{H_2O}\right) - RT\ln(10)\bullet pH$$

(4) $\mathrm{Ni(OH)_2} + 2\mathrm{H}^{+} \rightarrow \mathrm{Ni}^{2+} + 2\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{Ni(OH)_2}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{Ni(OH)_2}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - 2\mu\left(\mathrm{H_2O}\right) - 2RT\ln(10)\bullet pH$$

(5) $\mathrm{Ni(OH)_3^-} + 3\mathrm{H}^{+} \rightarrow \mathrm{Ni}^{2+} + 3\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{Ni(OH)_3^-}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{Ni(OH)_3^-}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - 3\mu\left(\mathrm{H_2O}\right) - 3RT\ln(10)\bullet pH$$

(6) $\mathrm{Ni(OH)_4^{2-}} + 4\mathrm{H}^{+} \rightarrow \mathrm{Ni}^{2+} + 4\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{Ni(OH)_4^{2-}}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{Ni(OH)_4^{2-}}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - 4\mu\left(\mathrm{H_2O}\right) - 4RT\ln(10)\bullet pH$$

(7) $\mathrm{NiOOH} + 3\mathrm{H}^{+} + e^- \rightarrow \mathrm{Ni}^{2+} + 2\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{NiOOH}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{NiOOH}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - 2\mu\left(\mathrm{H_2O}\right) - 3RT\ln(10)\bullet pH - F\bullet E_{\mathrm{SHE}}$$

(8) $\mathrm{NiO} + 2\mathrm{H}^{+} \rightarrow \mathrm{Ni}^{2+} + \mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{NiO}-\mathrm{Ni}^{2+}\right) = \mu\left(\mathrm{NiO}\right) - \mu\left(\mathrm{Ni}^{2+}\right) - \mu\left(\mathrm{H_2O}\right) - 2RT\ln(10)\bullet pH$$

(9) $\frac{1}{3}\mathrm{Ni_3O_4} + \frac{8}{3}\mathrm{H^+} + \frac{2}{3}e^- \rightarrow \mathrm{Ni^{2+}} + \frac{4}{3}\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{Ni_3O_4} - \mathrm{Ni^{2+}}\right) = \frac{1}{3}\mu\left(\mathrm{Ni_3O_4}\right) - \mu\left(\mathrm{Ni^{2+}}\right) - \frac{4}{3}\mu\left(\mathrm{H_2O}\right) - \frac{8}{3}RT\ln(10)\bullet pH - \frac{2}{3}F\bullet E_{\mathrm{SHE}}$$

(10) $\frac{1}{2}\mathrm{Ni_2O_3} + 3\mathrm{H^+} + e^- \rightarrow \mathrm{Ni^{2+}} + \frac{3}{2}\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{Ni_2O_3} - \mathrm{Ni^{2+}}\right) = \frac{1}{2}\mu\left(\mathrm{Ni_2O_3}\right) - \mu\left(\mathrm{Ni^{2+}}\right) - \frac{3}{2}\mu\left(\mathrm{H_2O}\right) - 3RT\ln(10)\bullet pH - F\bullet E_{\mathrm{SHE}}$$

(11) $\mathrm{NiO_2} + 4\mathrm{H^+} + 2e^- \rightarrow \mathrm{Ni^{2+}} + 2\mathrm{H_2O}$

$$\Delta\mu\left(\mathrm{NiO_2} - \mathrm{Ni^{2+}}\right) = \mu\left(\mathrm{NiO_2}\right) - \mu\left(\mathrm{Ni^{2+}}\right) - 2\mu\left(\mathrm{H_2O}\right) - 4RT\ln(10)\bullet pH - 2F\bullet E_{\mathrm{SHE}}$$

(D) Details of Experimental Buffer Solutions

pH	Titrant	pH Buffer	$[Ni^{2+}]$	Aeration	Other
	To Set pH	**To Control pH**	**To Control Ni^{2+} activity**	**Dissolved Oxygen**	**Electrolyte**
2.9	1 mM HCl	*non-buffered*	2 μM $NiCl_2$ *non-buffered*	Deaerated, N_2	0.9 M NaCl
4.9	0.48 M Triethylamine	0.15 M Citric Acid $C_6H_7O_7^- \leftrightarrow C_6H_6O_7^{2-}$	2 mM $NiCl_2$, $Ni^{2+} \leftrightarrow NiSO_4$	Deaerated, N_2	0.1 M H_2SO_4
5.4	0.6 M NaOH	0.25 M Citric Acid $C_6H_7O_7^- \leftrightarrow C_6H_6O_7^{2-}$	0.1 mM $NiCl_2$* *non-buffered*	Deaerated, N_2	—
8.4	—	0.114 M Boric Acid 0.021 M Sodium Tetraborate $H_3BO_3 \leftrightarrow H_2BO_3^-$	*non-buffered*	Deaerated, N_2	—
14	1 M NaOH	*non-buffered*	*non-buffered*	Quiescent aeration	—

Notes:

(i) All solutions are prepared with deionized water (18 MΩ-cm).

(ii) The asterisk (*) behind $NiCl_2$ at pH 5.4 indicates that $NiCl_2$ was added into the solution after the cathodic cleaning. Since $[Ni^{2+}]$ is not buffered at pH 5.4, in the course of the cathodic cleaning step, apart from the removal of the air-formed oxide from the Ni surface, it is also possible that Ni^{2+} ion may be reduced from solution into Ni metal on the surface.

(E) References

[1] M. W. Chase, *NIST-JANAF Thermochemical Tables (4th Ed.)* (American Institute of Physics, New York, 1998).

[2] M. Pourbaix, *ATLAS of Electrochemical Equilibria in Aqueous Solutions* (Pergamon Press, Oxford, 1966).

[3] J. Burgess, *Metal Ions in Solution* (Ellis Horwood Limited, Chichester, 1978).

[4] A. J. Bard, R. Parsons, and J. Jordan, *Standard Potentials in Aqueous Solution* (Marcel Dekker, New York, 1985).

[5] B. Beverskog and I. Puigdomenech, *Revised Pourbaix diagrams for nickel at 25-300 ℃*, Corrosion Science **39**, 969-980 (1997).