

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

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CONTENTS

(A) Structural Information	S2
(i) Lattice constants and angles of unit cells	S2
(ii) Atomic fractional coordinates in unit cells	S3
(iii) Supercells used in phonon calculations	S5
(B) Thermodynamic Energies	S6
(C) Reaction Paths and Chemical Potentials of Reaction	S8
(D) Details of Experimental Buffer Solutions	S10
(E) References	S11

(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	<i>Fm-3m</i> #225	1	$a/b/c = 2.475$ $\alpha/\beta/\gamma = 60.0$	2.448 60.0
NiO	<i>R-3m</i> #166	2	$a/c = 2.951$ $b = 5.093$ $\alpha = 106.84$ $\beta = 120.27$ $\gamma = 73.17$	2.920 5.006 106.96 120.00 73.04
Ni ₃ O ₄	<i>Fd-3m</i> #227	8	$a = 8.256$ $b = 8.093$ $c = 8.036$ $\alpha/\beta/\gamma = 90.0$	8.015 8.015 8.015 90.0
Ni ₂ O ₃	<i>R-3c</i> #167	2	$a/b/c = 5.166$ $\alpha/\beta/\gamma = 56.3$	5.165 55.49
NiO ₂	<i>P-3m1</i> #164	1	$a/b = 2.753$ $c = 4.636$ $\alpha/\beta = 90.0$ $\gamma = 120.0$	2.783 4.665 90.0 120.0
Ni(OH) ₂	<i>P-3m1</i> #164	1	$a/b = 3.129$ $c = 4.587$ $\alpha/\beta = 90.0$ $\gamma = 120.0$	3.115 4.395 90.0 120.0
NiOOH	<i>R-3m</i> #166	2	$a/b = 2.909$ $c = 9.705$ $\alpha = 90.0$ $\beta = 72.2$ $\gamma = 120.0$	2.913 9.424 90.0 72.0 120.0

(ii) Atomic fractional coordinates in unit cells

NiO, Space Group *R-3m* #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

Ni₃O₄, Space Group *Fd-3m* #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

Ni₂O₃, Space Group *R-3c* #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

NiO₂, Space Group *P-3m1* #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-3m1* #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-3m* #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 ₃ O ₄	2×2×2
Ni ₂ O 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 O₂ and H₂ molecules are calculated in a large vacuum-periodic supercell (15×15×15 Å³), which fully isolates these molecules from their periodic images.

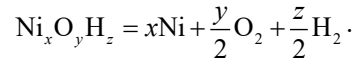
(B) Thermodynamic Energies

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 O₂ and H₂ gases). The G_T 's for the standard O₂ and H₂ 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, O₂, and H₂) can be written as



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

$$\Delta_f G = G_{tot}(\text{Ni}_x\text{O}_y\text{H}_z) - \left\{ xG_{tot}(\text{Ni}) + \frac{y}{2}G_{tot}(\text{O}_2) + \frac{z}{2}G_{tot}(\text{H}_2) \right\} = \Delta_f \varepsilon + \Delta G_T,$$

Where,

$$\Delta_f \varepsilon = \varepsilon(\text{Ni}_x\text{O}_y\text{H}_z) - \left\{ x\varepsilon(\text{Ni}) + \frac{y}{2}\varepsilon(\text{O}_2) + \frac{z}{2}\varepsilon(\text{H}_2) \right\}$$

is the electronic energy of formation, and

$$\Delta G_T = G_T(\text{Ni}_x\text{O}_y\text{H}_z) - \left\{ xG_T(\text{Ni}) + \frac{y}{2}G_T(\text{O}_2) + \frac{z}{2}G_T(\text{H}_2) \right\}$$

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 ₃ O ₄	0.469	0.315	1.211
Ni ₂ O 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^l) is calculated using

$$\mu^l = \mu^l_0 + RT \ln([I]),$$

where, R is the gas constant (8.314 J·mol⁻¹·K⁻¹); μ^l_0 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

$$\mu = RT \ln([H^+]) = -RT \ln(10) \cdot pH.$$

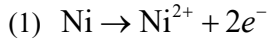
The μ_0^l 's (in eV/f.u.) of the considered Ni aqueous ions, as well as μ^s 's (in eV/f.u.) of Ni compounds, from the databases by Pourbaix [2], Burgess [3], Bard [4], and Beverskog [5] are listed below.

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 ₃ O ₄	-7.379	—	—	—
Ni ₂ O ₃	-4.869	—	—	—
NiO ₂	-2.230	—	—	-2.005
Ni(OH) ₂	-4.696	—	-4.696	-4.756
NiOOH	—	—	—	-3.406

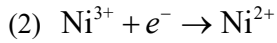
(C) Reaction Paths and Chemical Potentials of Reaction

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 ($= eN_A = 9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}$) 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.

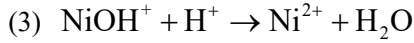
The chemical potentials of solids and aqueous ions as described in previous section are used here to calculate $\Delta\mu$'s, and it should be noted that the chemical potentials for aqueous ions are concentration dependent.



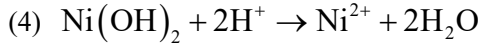
$$\Delta\mu(\text{Ni} - \text{Ni}^{2+}) = \mu(\text{Ni}) - \mu(\text{Ni}^{2+}) + 2F \cdot E_{\text{SHE}} = -\mu(\text{Ni}^{2+}) + 2F \cdot E_{\text{SHE}}$$



$$\Delta\mu(\text{Ni}^{3+} - \text{Ni}^{2+}) = \mu(\text{Ni}^{3+}) - \mu(\text{Ni}^{2+}) - F \cdot E_{\text{SHE}}$$



$$\Delta\mu(\text{NiOH}^+ - \text{Ni}^{2+}) = \mu(\text{NiOH}^+) - \mu(\text{Ni}^{2+}) - \mu(\text{H}_2\text{O}) - RT \ln(10) \cdot pH$$



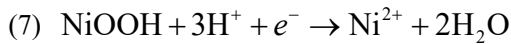
$$\Delta\mu(\text{Ni}(\text{OH})_2 - \text{Ni}^{2+}) = \mu(\text{Ni}(\text{OH})_2) - \mu(\text{Ni}^{2+}) - 2\mu(\text{H}_2\text{O}) - 2RT \ln(10) \cdot pH$$



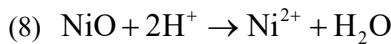
$$\Delta\mu(\text{Ni}(\text{OH})_3^- - \text{Ni}^{2+}) = \mu(\text{Ni}(\text{OH})_3^-) - \mu(\text{Ni}^{2+}) - 3\mu(\text{H}_2\text{O}) - 3RT \ln(10) \cdot pH$$



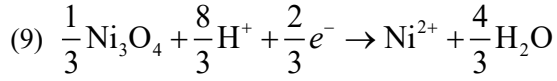
$$\Delta\mu(\text{Ni}(\text{OH})_4^{2-} - \text{Ni}^{2+}) = \mu(\text{Ni}(\text{OH})_4^{2-}) - \mu(\text{Ni}^{2+}) - 4\mu(\text{H}_2\text{O}) - 4RT \ln(10) \cdot pH$$



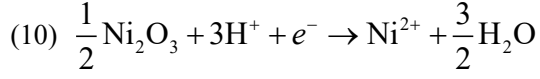
$$\Delta\mu(\text{NiOOH} - \text{Ni}^{2+}) = \mu(\text{NiOOH}) - \mu(\text{Ni}^{2+}) - 2\mu(\text{H}_2\text{O}) - 3RT \ln(10) \cdot pH - F \cdot E_{\text{SHE}}$$



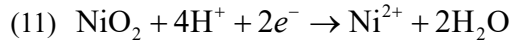
$$\Delta\mu(\text{NiO} - \text{Ni}^{2+}) = \mu(\text{NiO}) - \mu(\text{Ni}^{2+}) - \mu(\text{H}_2\text{O}) - 2RT \ln(10) \cdot pH$$



$$\Delta\mu(\text{Ni}_3\text{O}_4 - \text{Ni}^{2+}) = \frac{1}{3} \mu(\text{Ni}_3\text{O}_4) - \mu(\text{Ni}^{2+}) - \frac{4}{3} \mu(\text{H}_2\text{O}) - \frac{8}{3} RT \ln(10) \bullet pH - \frac{2}{3} F \bullet E_{\text{SHE}}$$



$$\Delta\mu(\text{Ni}_2\text{O}_3 - \text{Ni}^{2+}) = \frac{1}{2} \mu(\text{Ni}_2\text{O}_3) - \mu(\text{Ni}^{2+}) - \frac{3}{2} \mu(\text{H}_2\text{O}) - 3RT \ln(10) \bullet pH - F \bullet E_{\text{SHE}}$$



$$\Delta\mu(\text{NiO}_2 - \text{Ni}^{2+}) = \mu(\text{NiO}_2) - \mu(\text{Ni}^{2+}) - 2\mu(\text{H}_2\text{O}) - 4RT \ln(10) \bullet pH - 2F \bullet E_{\text{SHE}}$$

(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	<i>non-buffered</i>	2 μM NiCl ₂ <i>non-buffered</i>	Deaerated, N ₂	0.9 M NaCl
4.9	0.48 M Triethylamine	0.15 M Citric Acid C ₆ H ₇ O ₇ ⁻ ↔ C ₆ H ₆ O ₇ ²⁻	2 mM NiCl ₂ , Ni ²⁺ ↔ NiSO ₄	Deaerated, N ₂	0.1 M H ₂ SO ₄
5.4	0.6 M NaOH	0.25 M Citric Acid C ₆ H ₇ O ₇ ⁻ ↔ C ₆ H ₆ O ₇ ²⁻	0.1 mM NiCl ₂ [*] <i>non-buffered</i>	Deaerated, N ₂	—
8.4	—	0.114 M Boric Acid 0.021 M Sodium Tetraborate H ₃ BO ₃ ↔ H ₂ BO ₃ ⁻	<i>non-buffered</i>	Deaerated, N ₂	—
14	1 M NaOH	<i>non-buffered</i>	<i>non-buffered</i>	Quiescent aeration	—

Notes:

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

(ii) The asterisk (*) behind NiCl₂ at pH 5.4 indicates that NiCl₂ was added into the solution after the cathodic cleaning. Since [Ni²⁺] 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 Ni²⁺ 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 °C*, *Corrosion Science* **39**, 969-980 (1997).