The Role of Carbonate in Electro-catalytic water oxidation by Ni(1,4,8,11-tetraazacyclotetra-decane)$^{2+}$

Burg Ariela*, Wolfer Yaniv, Shamir Dror, Kornweitz Haya, Albo Yael, Maimon Eric, Meyerstein Dan.

Supporting information:

S-1 Electrochemistry methods: The electrochemical results were obtained with a pocketSTAT instrument (Ivium Technologies). The experiments were done in an electrochemical cell that included a glassy carbon electrode, 3.0 mm^2, as a working electrode, *vs*. Ag/AgCl electrode and a Pt electrode as a counter electrode. Ionic strength of 0.20 M was controlled by adding $NaClO_4$, Ar atmosphere. Two methods were used: cyclic voltammetry and controlled potential electrolysis. All values are the average of at least three independent experiments.

S-2 XPS measurements: XPS data were collected using an X-ray photoelectron spectrometer ESCALAB 250 ultrahigh vacuum (1×10^{-9} bar) apparatus with an AlK^{α} X-ray source and a monochromator. The X-ray beam size was 500 µm. Surveyed spectra were recorded with pass energy (PE) 150 eV, and high-energy resolution spectra were recorded with pass energy (PE) 20 eV. To correct for charging effects, all spectra were calibrated relative to a carbon C 1s peak positioned at 284.8 eV. Processing of the XPS results was carried out using the AVANTGE program.

S-3 Rugged Dissolved Oxygen (RDO): An optical electrode (Eutech Instruments) was used to identify dissolved O_2.

S-4 DFT calculations: All calculations were performed using the G09 program.[1] Geometry optimizations in the B3LYP exchange-correlation functional of DFT theory were performed using the 6-311+G** basis set for all atoms. The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions, and to determine the reactants and products associated with each transition-state structure (by following the normal modes associated with imaginary frequencies). The transition state structures were optimized using the “opt=QST3” keyword. Solvation effects were calculated using the SMD method[1]. For each structure, the free energy was calculated. This calculation takes into account the ZPE and thermal correction. The program's default standard state corresponding to an ideal gas at a standard pressure of 1 atm was changed to

use either a standard state of 1 M (most species) or of 55.5 M (for water molecules). When other concentrations (C) were used, further corrections were applied according to the equation: RTlnC. The free energy values of the structures were used to calculate ΔG^0 values for the relevant reactions. The calculations were performed under similar conditions to those used for the electrochemical experiment.

S-5 Materials: AR grade sodium perchlorate and perchloric acid were purchased from Aldrich. The ligand L_2= 1,4,8,11-tetraazacyclotetradecane and the complex $Ni^{II}L_2(ClO_4)_2$ were synthesized by a previously reported method.[2] Before a series of experiments, the spectrum of the $Ni^{II}L_2(ClO_4)_2$ complex solution was measured (Fig. 7 in the article). Before each electrochemical experiment, the CV of the $Ni^{II}L_2(ClO_4)_2$ complex solution was measured (black graph in Fig. 2). The spectrum and the CV that were obtained are typical for a $Ni^{II}L_2(ClO_4)_2$ complex solution and are identical to published results.

All the solutions were prepared in deionized water that was further purified by passing through a Milli Q Millipore setup, final resistivity >10 MΩ/cm. Ar from Maxima was used to de-aerate the solutions.

After controlled potential experiments the solutions were filtered by 1kDa ultrafilter discs (1KDa ultrafiltration disc, from Millipore). The discs were measured by XPS.

S – 6 Analysis of L_2.

- Elemental analysis:

The results of the elemental analysis are summed up in the following table:

Table S-1 - C, H, N, composition by elemental analysis:

	% Experimental results	% Theoretical
C	59.88 %	59.95 %
H	27.68 %	12. 08 %
N	12.17 %	27.97 %

- ^{13}C-NMR spectra of L_2 was measured by DMX 500 bruker instrument. The spectrum is shown in Fig. S-4.

,

Table S-2- DFT Results for different reactions:

Reaction No.*	Reaction	L_1 (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetra-decane) L_2 (1,4,8,11-tetraazacyclotetra-decane)	ΔG^o (kcal/mol)	comments
6	$Ni^{IV}L(PO_4)_2^{2-} + H_2O \rightarrow Ni^{IV}L(PO_4)OH + HPO_4^{2-}$	L_2	-10.19	exoergic
		L_1	-14.02	
7	$Ni^{IV}L(PO_4)_2^{2-} + H_3O^+ \rightarrow Ni^{IV}L(PO_4)HPO_4^- + H_2O$	L_2	-18.97(pH 7)	exoergic
8	$Ni^{IV}L(PO_4)HPO_4^- \rightarrow Ni^{IV}L(PO_4)OH + PO_3^-$	L_2	-0.4	exoergic or thermo-neutral
S-1	$Ni^{IV}L(PO_4)_2^{2-} + H_2O \rightarrow Ni^{IV}L(PO_4)O^- + H_2PO_4^-$	L_2	9.76	endoergic
		L_1	8.38	
S-2	$Ni^{IV}L(HPO_4)_2 + H_2O + HPO_4^{2-} \rightarrow Ni^{IV}L(HPO_4)O + 2H_2PO_4^-$	L_2	8.41	endoergic
		L_1	16.39	
S-3	$Ni^{IV}L(HPO_4)_2 + H_2O \rightarrow Ni^{IV}L(HPO_4)OH^+ + H_2PO_4^-$	L_2	-4.98	exoergic or thermo-neutral
		L_1	1.23	
11	$Ni^{IV}L(CO_3)_2 + H_2O \rightarrow Ni^{IV}L(CO_3)OH^+ + HCO_3^-$	L_2	-10.33	exoergic
S-4	$Ni^{IV}L(CO_3)_2 + H_2O + CO_3^{2-} \rightarrow Ni^{IV}L(CO_3)O + 2HCO_3^-$	L_2	2.51	Slightly endoergic
S-5	$Ni^{IV}L(HCO_3)_2^{2+} + H_2O + CO_3^{2-} \rightarrow Ni^{IV}L(HCO_3)OH^{2+} + 2HCO_3^-$	L_2	-23.72	exoergic
S-6	$Ni^{IV}L(HCO3)_2^{2+} + H_2O + 2CO_3^{2-} \rightarrow Ni^{IV}L(HCO_3)O^+ + 3HCO_3^-$	L_2	-21.67	exoergic

* S-number – a reaction that is not shown in the article.

In order to validate our DFT calculation, pKa values of $H_2PO_4^-$ and HCO_3^- were calculated. The results are shown in table 3, a very good agreement to experimental values was observed.

Table S-3: pKa values of $H_2PO_4^-$ and HCO_3^-

	calculated	experimental
$H_2PO_4^-$	6.39	7.2
HCO_3^-	11.11	10.32

The experimental values of K_a that were used: $H_2PO_4^-$ - 6.23×10^{-8} [3], HCO_3^- - 4.69×10^{-11} [3]

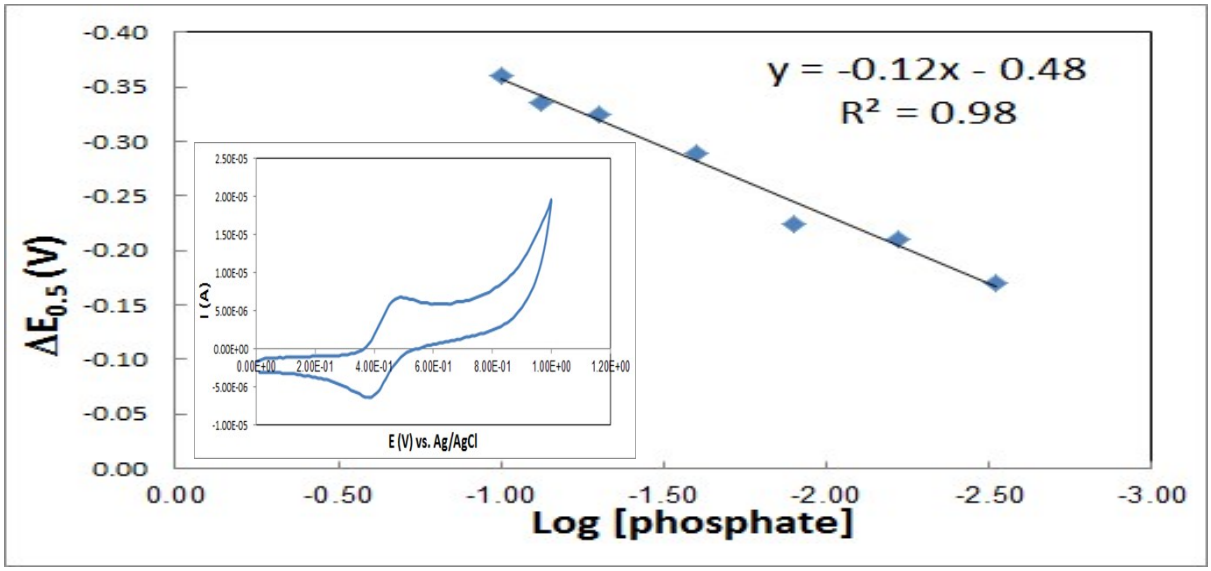

Figure S-1 – $\Delta E_{0.5}$ as a function of Log[phosphate]. Solutions contain $Ni^{II}L_2^{2+}$ 1.0×10^{-3} M and different concentrations of PO_4^{3-} (0 – 1.25×10^{-2} M $HPO_4^{2-}/H_2PO_4^-$. At pH 7.0, 50 mV/s. Ionic strength 0.20 M controlled by adding $NaClO_4$. A glassy carbon electrode was used as the working electrode, *vs*. Ag/AgCl, Pt as the counter electrode, Ar atmosphere. Inset: cyclic voltammetry of solution that contains $Ni^{II}L_2^{2+}$ 1.0×10^{-3} M, 0.10 M $HPO_4^{2-}/H_2PO_4^-$ at pH 7.0, 50 mV/s.

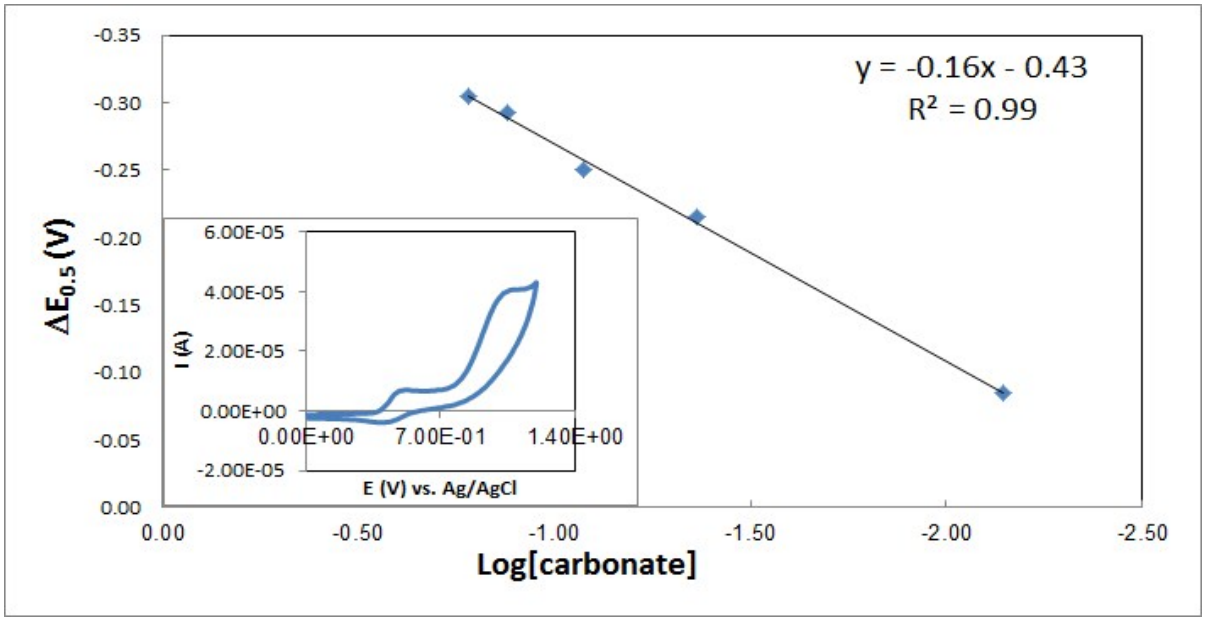

Figure S-2 – $\Delta E_{0.5}$ as a function of Log[carbonate]. Solutions contain $Ni^{II}L_2^{2+}$ 1.0×10^{-3} M and different concentrations of HCO_3^-. At pH 7.0, 50 mV/s. Ionic strength 0.20 M controlled by adding $NaClO_4$, A glassy carbon electrode was used as the working electrode, *vs*. Ag/AgCl, Pt as the counter electrode, Ar atmosphere. Inset: cyclic voltammetry of solution containing $Ni^{II}L_2^{2+}$ 1.0×10^{-3} M, 0.20 M HCO_3^- at pH 7.0, 50 mV/s.

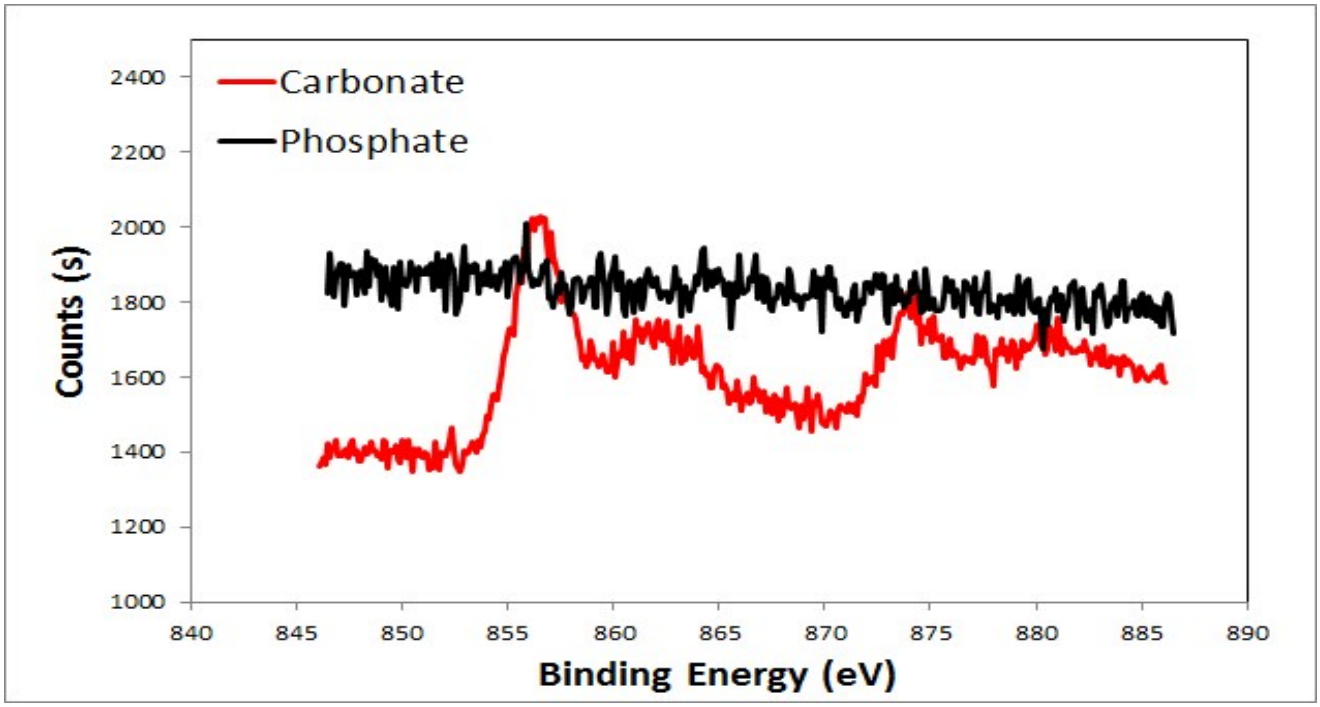

Figure S-3 - XPS results after controlled potential experiments (Solution composition in the controlled potential experiments: —— $Ni^{II}L_2^{2+}$ 1.0×10^{-3} M, $NaHCO_3$ 0.20 M, pH 7.0. —— $Ni^{II}L_2^{2+}$ 1.0×10^{-3} M, HPO_4^{2-}/$H_2PO_4^-$. 0.0125 M, pH 7.0. A glassy carbon electrode was used as the working electrode, *vs*. Ag/AgCl, Pt as the counter electrode, V = 1.3 V, ionic strength 0.20 M controlled by adding $NaClO_4$, Ar atmosphere, during 20 h). The glassy carbon electrodes were cleaned with a cleaning paper suitable for GC electrodes. The experiment solutions were filtered by 1kDa ultrafilter discs, and the papers and discs were measured by XPS.

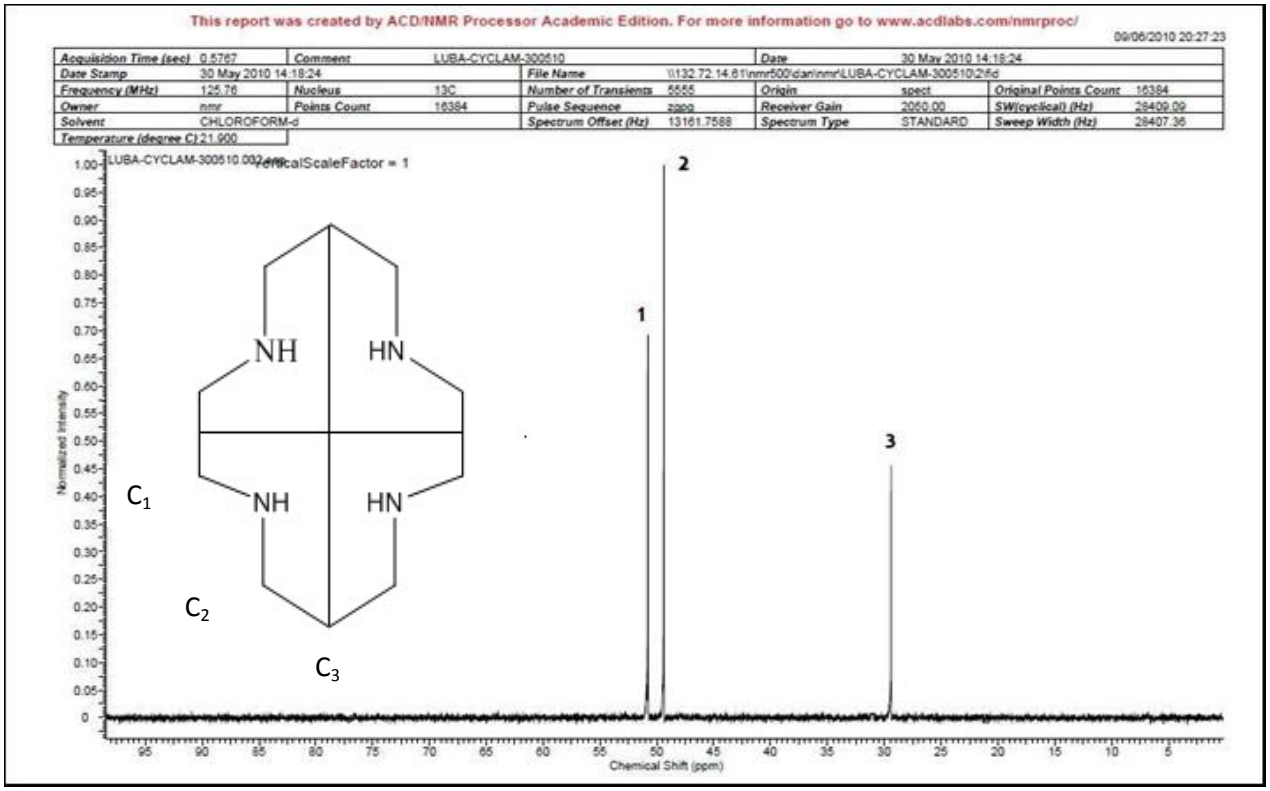

Figure S-4 – C-NMR results for L_2 which is dissolved in $CDCl_3$.

The literature results for C-NMR[4] ($\delta(C_1)$ = 50 ppm, $\delta(C_2)$ = 48.5 ppm$\delta(C_3)$ = 28.4 ppm) indicate that we work with a purity material.

References

1. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *Journal of Physical Chemistry B*, 2009, 113, 6378-6396. .
2. E. K. Barefield;, F. Wagner;, A. W. Herlinger; and A. R. Dahl;, *Inorganic Syntheses*, 1976, 16, 220-225.
3. A. Prevedello, I. Bazzan, N. Dalle Carbonare, A. Giuliani, S. Bhardwaj, C. Africh, C. Cepek, R. Argazzi, M. Bonchio and S. Caramori, *Chemistry - An Asian Journal* 2016, 11, 1281-1287. .
4. A. Prokhorov, N. Le Bris, H. Bernard, G. Claudon and H. Handel, *Synthetic Communications*, 2006, 36, 3271-3282.