

# ChemSusChem

## Supporting Information

### **Potential- and Buffer-Dependent Catalyst Decomposition during Nickel-Based Water Oxidation Catalysis**

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## 1. Materials and methods

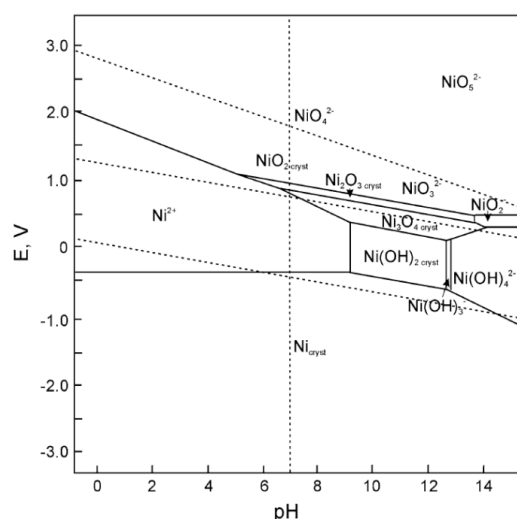
All reagents were purchased from commercial suppliers and used without further purification. The  $[\text{Ni}^{\text{II}}(\text{meso-L})](\text{ClO}_4)_2$  complex was prepared in a three step procedure according to literature and spectroscopic analysis was in line with the reported values.<sup>1,2</sup> Fluorine doped tin oxide (FTO) electrodes were cleaned according to literature procedure.<sup>3</sup> Milli-Q Ultrapure grade water ( $> 18.2 \text{ M}\Omega \text{ cm}$  resistivity) was used for all experiments and for the preparation of aqueous buffer solutions.

## 2. Electrochemical methods

Controlled potential electrolysis (CPE) measurements and electrochemical quartz crystal microbalance (EQCM) measurements were recorded on an Autolab PG-STAT302N potentiostat with a three electrode system. For CPE measurements without EQCM, a FTO working electrode was used, a platinum coil counter electrode and a leak free Ag/AgCl reference electrode was used. For EQCM measurements during CPE, a gold coated quartz working electrode, a gold coil counter electrode and a leak free Ag/AgCl reference electrode was used. For XPS measurements after CPE, the electrodes were taken out immediately after electrolysis and washed with deionized water for 10 s. For experiments with pH tuning, the pH was adjusted to 8.5 just before ending electrolysis by addition of a NaOH solution. The binding energy in XPS was calibrated with respect to the C 1s level 284.6 eV of contaminated carbon. For CPE experiments with  $\text{Ni}(\text{NO}_3)_2$  in a 0.1 M pH 7 phosphate buffer, a fresh solution was prepared for each experiment, and no precipitate was observed during any of our experiments.

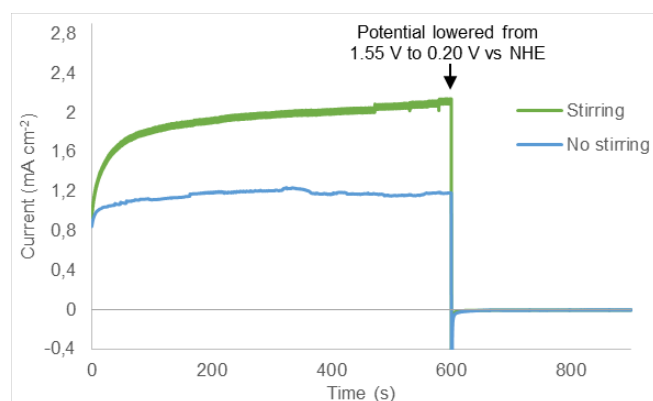
## 3. Additional data and Figures

### 3.1 Pourbaix diagram of nickel



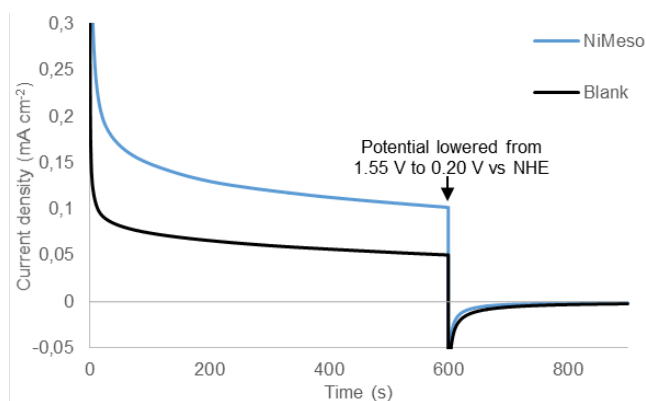
Supporting Information Figure S1. Pourbaix diagram of nickel in water.<sup>4</sup>

### 3.2 CPE of nickel nitrate in a pH 7 phosphate buffer

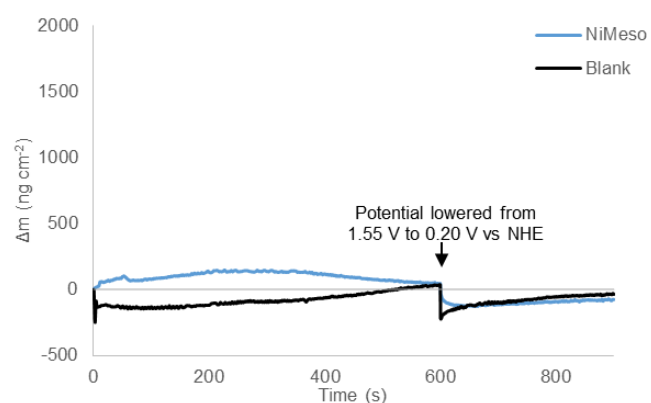


Supporting Information Figure S2. Controlled potential electrolysis measurements at 1.55 V vs NHE for 2500 s followed by 300 s at 0.2 V vs NHE of 1 mM  $\text{Ni}(\text{NO}_3)_2$  while stirring (800 rpm, green) and while not stirring (blue) in a 0.1 M pH 7 phosphate buffer using a FTO working electrode.

### 3.3 CPE and EQCM of NiMeso in a pH 7 acetate buffer

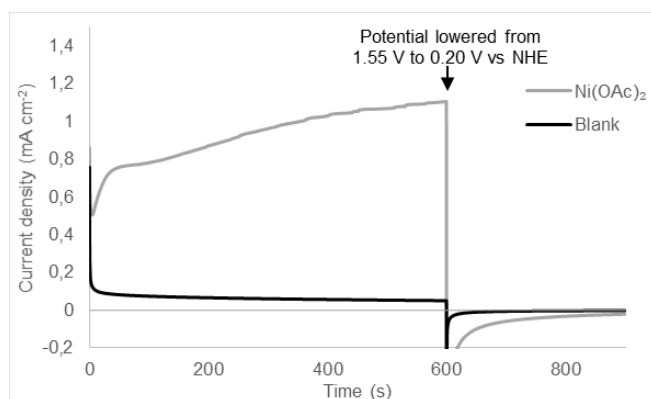


**Supporting Information Figure S3.** Controlled potential electrolysis measurements at 1,55 V vs NHE for 600 s followed by 300 s at 0,2 V vs NHE of the buffer solution (black) and 1 mM **NiMeso** (blue) in a 0,1 M pH 7 acetate buffer using a gold working electrode.

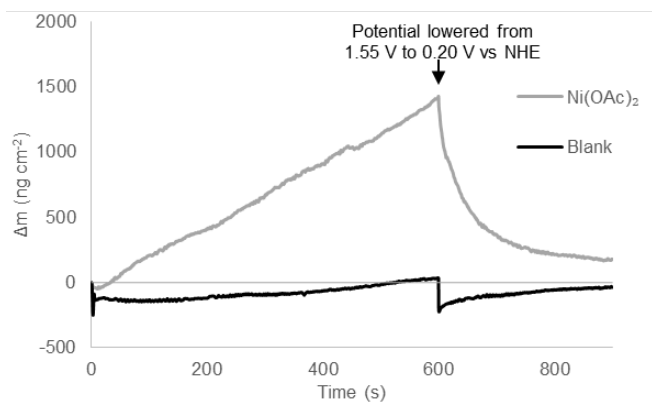


**Supporting Information Figure S4.** Electrochemical quartz microbalance measurements at 1,55 V vs NHE for 600 s followed by 300 s at 0,2 V vs NHE of the buffer solution (black) and 1 mM **NiMeso** (blue) in a 0,1 M pH 7 acetate buffer using a gold working electrode.

### 3.4 CPE and EQCM of nickel acetate in a pH 7 acetate buffer



**Supporting Information Figure S5.** Controlled potential electrolysis measurements at 1,55 V vs NHE for 600 s followed by 300 s at 0,2 V vs NHE of the buffer solution (black) and 1 mM Ni(OAc)<sub>2</sub> (gray) in a 0,1 M pH 7 acetate buffer using a gold working electrode.



**Supporting Information Figure S6.** Electrochemical quartz microbalance measurements at 1.55 V vs NHE for 600 s followed by 300 s at 0.2 V vs NHE of the buffer solution (black) and 1 mM  $\text{Ni(OAc)}_2$  (gray) in a 0.1 M pH 7 acetate buffer using a gold working electrode.

#### 4. References

- [1] A. M. Tait, D. H. Busch in *Inorganic Syntheses, Vol. XVIII* (Eds.: B. E. Douglas), John Wiley & Sons, Inc., **1978**, pp. 2-6.
- [2] A. M. Tait, D. H. Busch in *Inorganic Syntheses, Vol. XVIII* (Eds.: B. E. Douglas), John Wiley & Sons, Inc., **1978**, pp. 10-13.
- [3] M. Zhang, M. T. Zhang, C. Hou, Z. F. Ke, T. B. Lu, *Angew. Chem. Int. Ed.* **2014**, *126*, 13258-13264; *Angew. Chem. Int. Ed.* **2014**, *53*, 13042-13048.
- [4] F. Ciesielczyk, P. Bartczak, K. Wieszczycka, K. Siwińska-Stefańska, M. Nowacka, T. Jesionowski, *Adsorption* **2013**, *19*, 423-434.