Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Electrification of the glucose valorization over NiO/Ni foam

Giancosimo Sanghez de Luna, [a] Tommaso Tabanelli, [a, b] Juan J. Velasco-Vélez, [c, d] Eleonora Monti, [a] Francesca Ospitali, [a] Stefania Albonetti, [a, b] Fabrizio Cavani, [a, b] Giuseppe Fornasari, [a ,b] Patricia Benito* [a, b]

[a.] *Dipartimento Chimica Industriale "Toso Montanari", Alma Mater Studiorum-Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italy*
[b.] *Center for Chemical Catalysis – C3, Alma Mater Studiorum – Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italy*
[c.] *ALBA Synchrotron Light Source, 08290 Cerdanyola del Vallés (Barcelona), Spain*
[d.] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*
*patricia.benito3@unibo.it

Chemicals

The chemicals used were sodium hydroxide (≥98%, Sigma-Aldrich), nickel nitrate hexahydrate (99.9985%, Alfa Aesar), ammonium chloride (>99.5%, Sigma-Aldrich), nickel chloride hexahydrate (Sigma-Aldrich), D-glucose anhydrous (99%, Alfa Aesar), D-gluconic acid sodium salt (97%, Sigma-Aldrich), D-fructose (99%, Alfa Aesar).

Analytical standard used for High Performance Liquid Chromatography (HPLC) analysis were: D-saccharic acid potassium salt (glucaric acid, 98%, Sigma-Aldrich), D-glucuronic acid (>98%, Sigma-Aldrich), oxalic acid anhydrous (98%, Acros Organics), sodium mesoxalate monohydrate (>98%, Sigma-Aldrich), D-arabinose (99%, Alfa Aesar), D-Mannose (99%, Alfa Aesar), 5-keto-D-gluconic acid potassium salt (98%, Alfa Aesar), 2-keto-D-gluconic acid hemicalcium salt monohydrate (99%, Alfa Aesar), DL-tartaric acid (99%, Alfa Aesar), tartronic acid (>97%, Sigma–Aldrich), glycolic acid (98%, Alfa Aesar), L-glyceric acid hemicalcium salt monohydrate (>97%, Sigma-Aldrich), formic acid pure (98+%, Acros Organics). All chemicals were used without further purification. Ultrapure water, UPW, (18 MΩ*cm) was used for the preparation of all aqueous solutions.

Analysis of the products

It should be noted that, due the occurrence of isomerization of glucose, the presence of fructose was identified in the solutions before and after reaction, therefore the amount of unreacted (consumed) glucose after electrolyses was corrected adding the amount of fructose detected.

In the chromatograms acquired, the overlap between the peaks of glucose and gluconic acid occurred on both RID and DAD detectors. However, glucose has a negligible response factor to DAD compared to gluconic acid, while the response factors to RID are of the same order of magnitude. Therefore, it was assumed that the peak visible at DAD detector can be exclusively attributed to gluconic acid. Hence, the amount of gluconic acid was easily obtained from DAD detector:

$$C_{gluconic\ acid} = \frac{A_{GO,DAD}}{f_{GO,DAD}}$$

Then, its equivalent area on RID was calculated using the related response factor, $f_{GO,RID}$:

$$A_{GO,RID} = C_{gluconic\ acid} * f_{GO,RID}$$

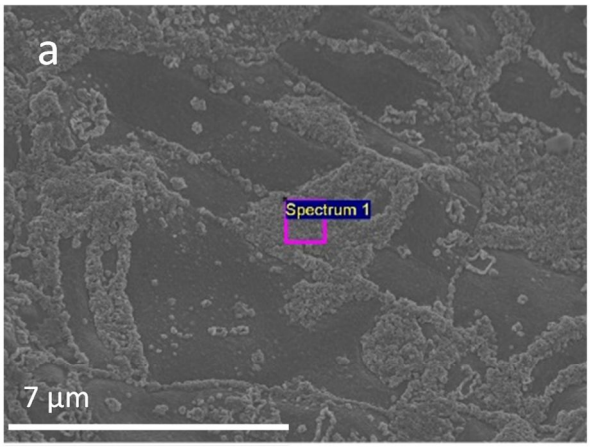
Finally, the area of glucose peak and therefore its residual concentration were obtained by subtracting $A_{GO,RID}$ from the peak containing the glucose+gluconic acid, A_{RID}:

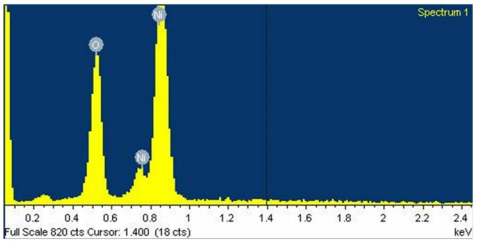
$$C_{glucose} = \frac{A_{RID} - A_{GO,RID}}{f_{glu,RID}}$$

where: C = concentration; $A_{GO,DAD}$ = area of gluconic acid peaks from DAD; $f_{GO,DAD}$ = response factor of gluconic acid at DAD; $A_{GO,RID}$ area of gluconic acid peaks from RID; $f_{GO,RID}$ = response factor of gluconic acid at RID; A_{RID} = total area of peak from RID (glucose+gluconic acid); $f_{glu,RID}$ = response factor of glucose at RID. This procedure was validated by injecting different standard mixtures of glucose and gluconic acid at different concentrations and evaluating the difference between the sum of the individual areas and the peak recorded on the chromatogram.

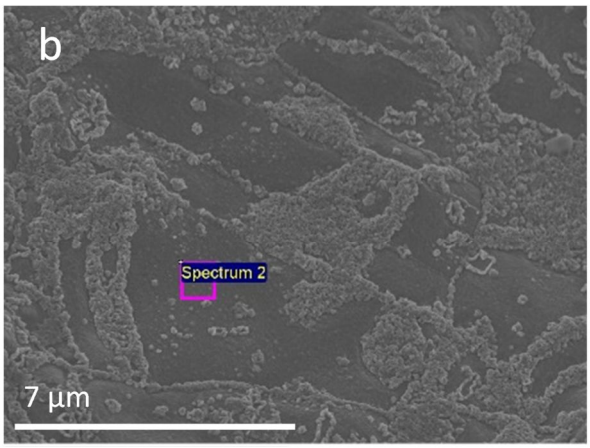
Similarly, arabinose and glyceric acid showed the same retention time on chromatograms, with the negligible signal of arabinose at DAD compared to glyceric acid. Nevertheless, the procedure used above for glucose and gluconic acid did not bring any satisfactory result in this case. Hence, since the two compounds have a response of the same order of magnitude at RID, the quantification was carried out by making an

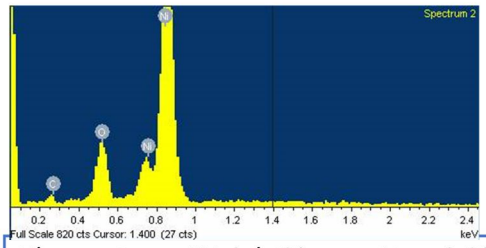
average of the respective f, thus not distinguishing the contribution of the single compounds. Their concentration will be indicated below as $C_{arabinose/glyceric\ acid}$.



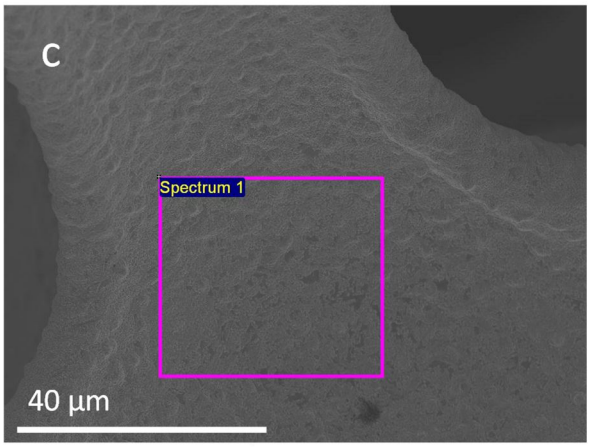


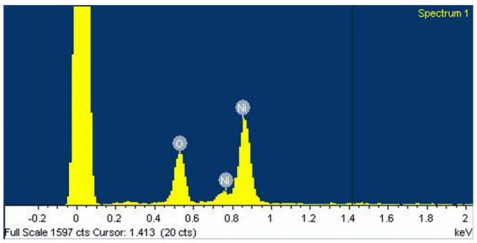
Element	Weight%	Atomic%
O K	20.22	48.19
Ni L	79.78	51.81
Totals	100.00	





Element	Weight%	Atomic%
C K	1.11	4.29
O K	8.23	23.91
Ni L	90.66	71.80
Totals	100.00	





Element	Weight%	Atomic%
O K	19.25	46.66
Ni L	80.75	53.34
Totals	100.00	

Figure S1. SEM/EDS characterization of the NiO/Ni foam: a) small coating with NiO particles; b) region without NiO particles; c) large coating with NiO particles. The presence of oxygen was proved all over the foam surface despite the absence of the particles.

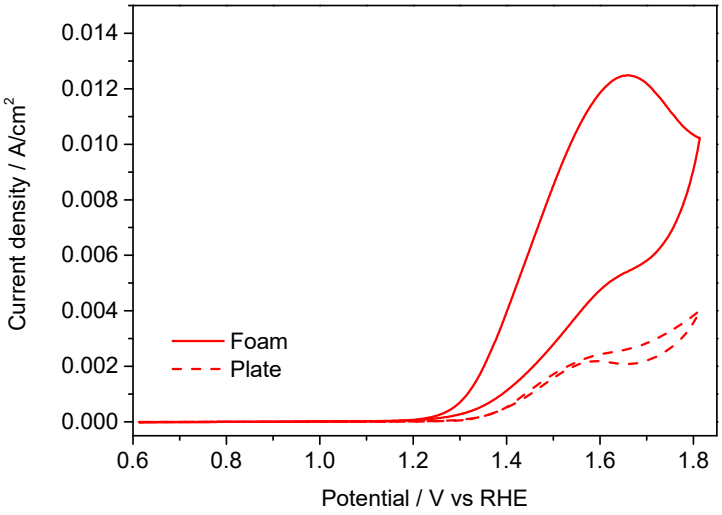


Figure S2. Comparison of the CVs recorded at Ni foam and plate in the 0.05 M glucose in 0.1 M NaOH electrolyte. Conditions: 0.6 - 1.8 V vs RHE; scan rate 5 mV s^{-1}.

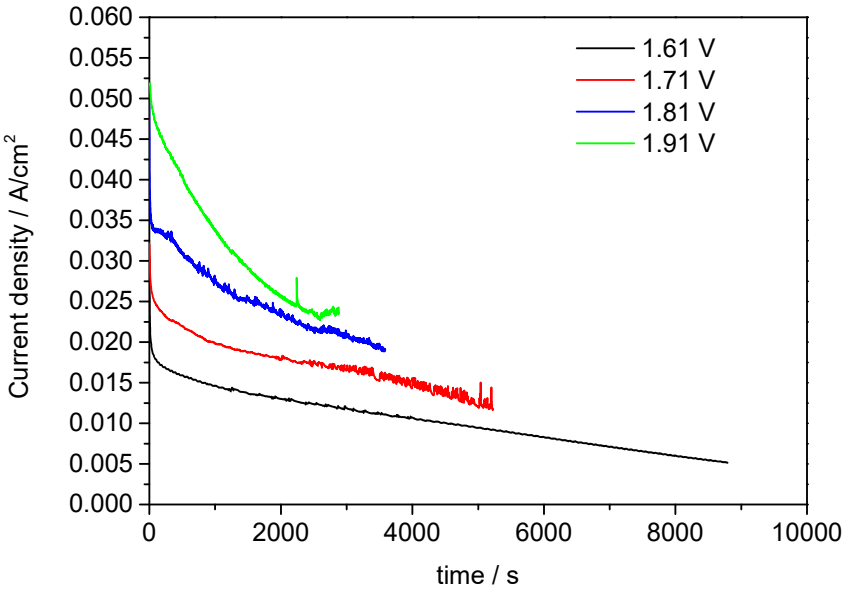


Figure S3. Evolution of the current density during electrooxidations of glucose 0.05 M electrolytes in NaOH 0.1 M at different potentials (1.61, 1.71, 1.81, and 1.91 V vs RHE).

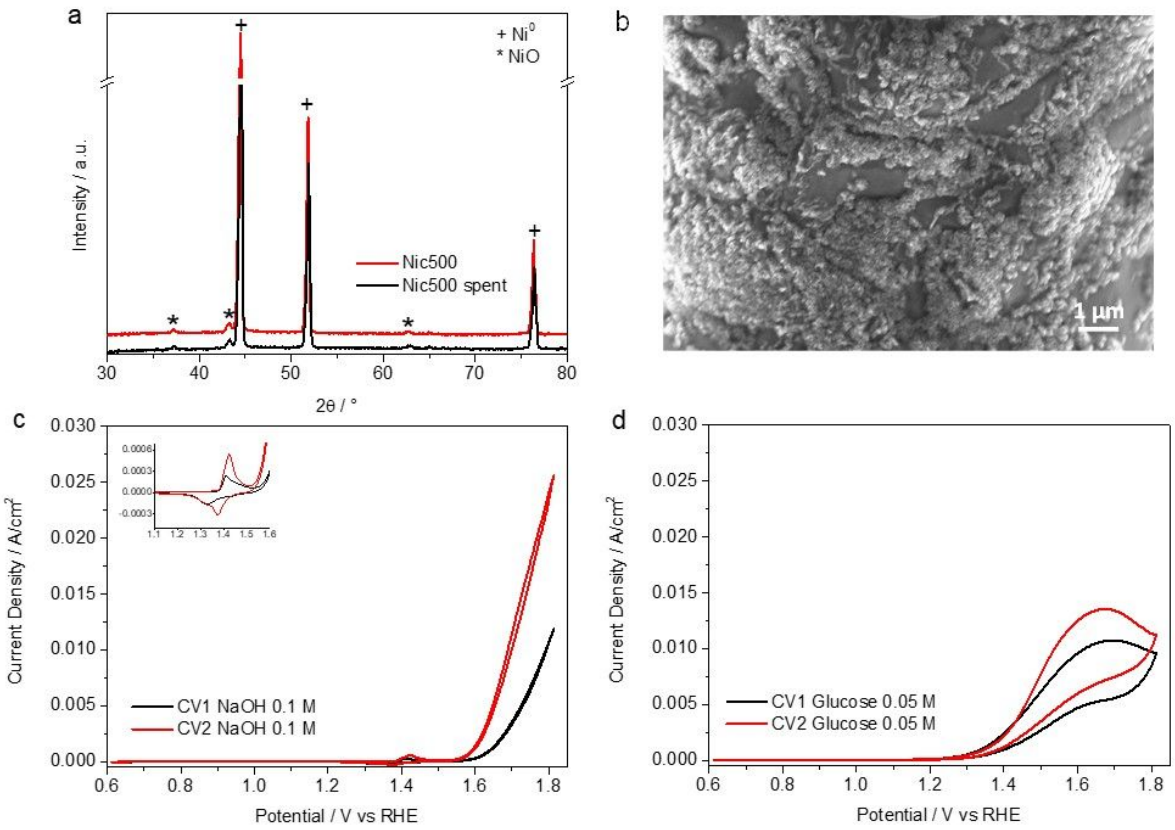


Figure S4. Characterization of spent catalyst tested at 1.81 V vs RHE in a 0.05 M glucose in NaOH 0.1 M electrolyte, for comparison purposes the characterization of the fresh catalyst is included: a) XRD patterns; b) SEM image of the surface of the foam; c) CVs in NaOH 0.1 M; and d) CVs in 0.05 M glucose in NaOH 0.1 M.

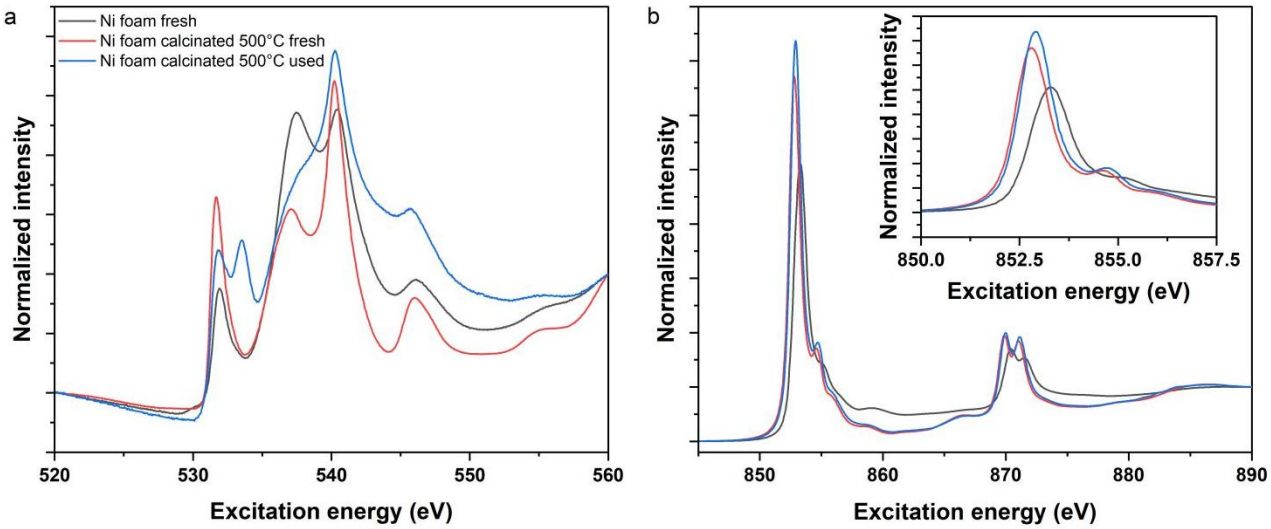


Figure S5. XAS spectra a) O K-edge and b) Ni $L_{2,3}$ edges of Ni foam fresh, calcined at 500°C before reaction and calcined at 500 °C after reaction. The spent catalyst was tested at 1.81 V vs RHE in a 0.05 M glucose in NaOH 0.1 M electrolyte

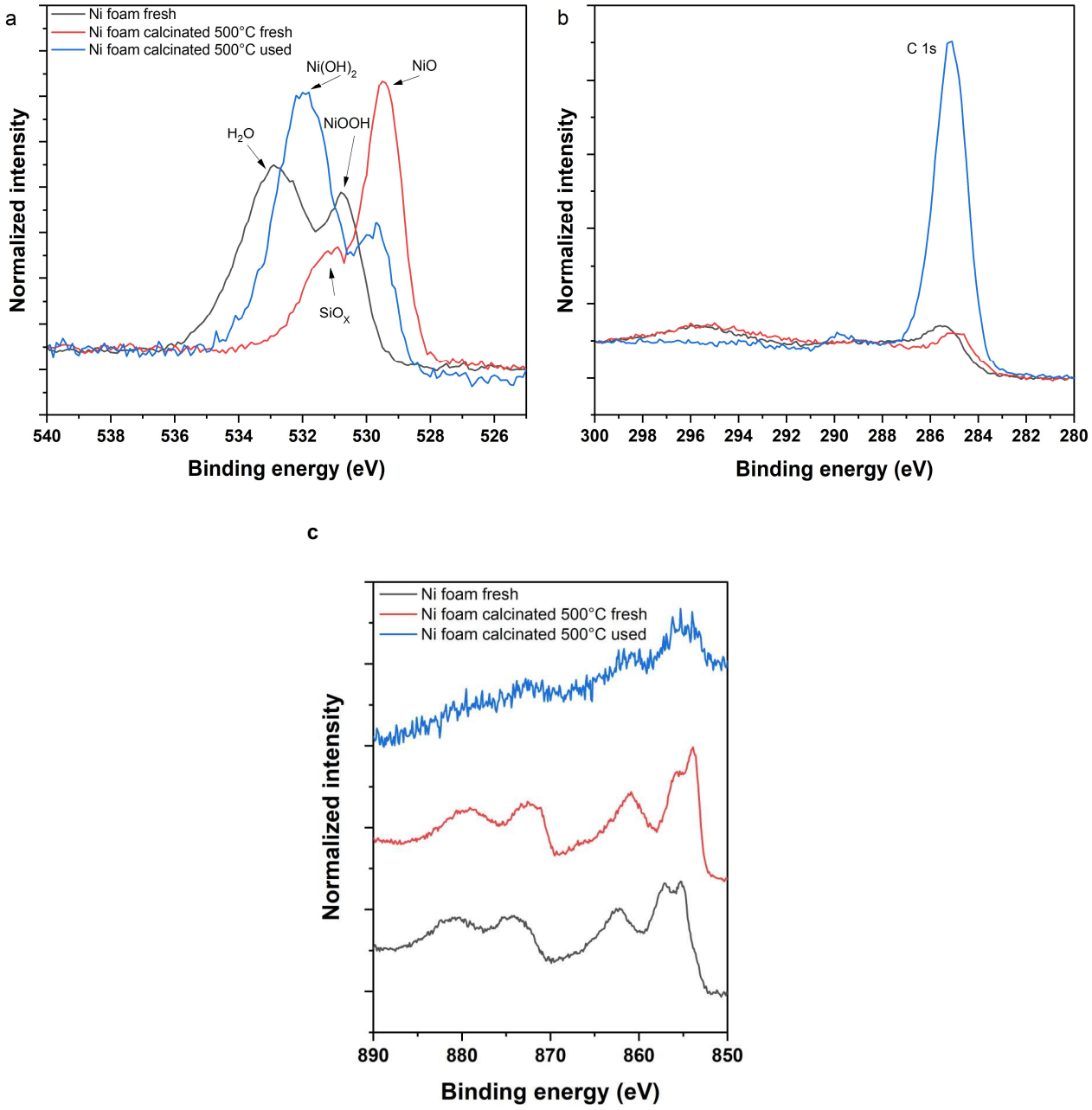


Figure S6. XPS spectra a) O 1*s*, b) C 1*s* and Ni 2*p* of Ni foam fresh, calcined at 500°C before reaction and calcined at 500°C after reaction. The spent catalyst was tested at 1.81 V vs RHE in a 0.05 M glucose in NaOH 0.1 M electrolyte.

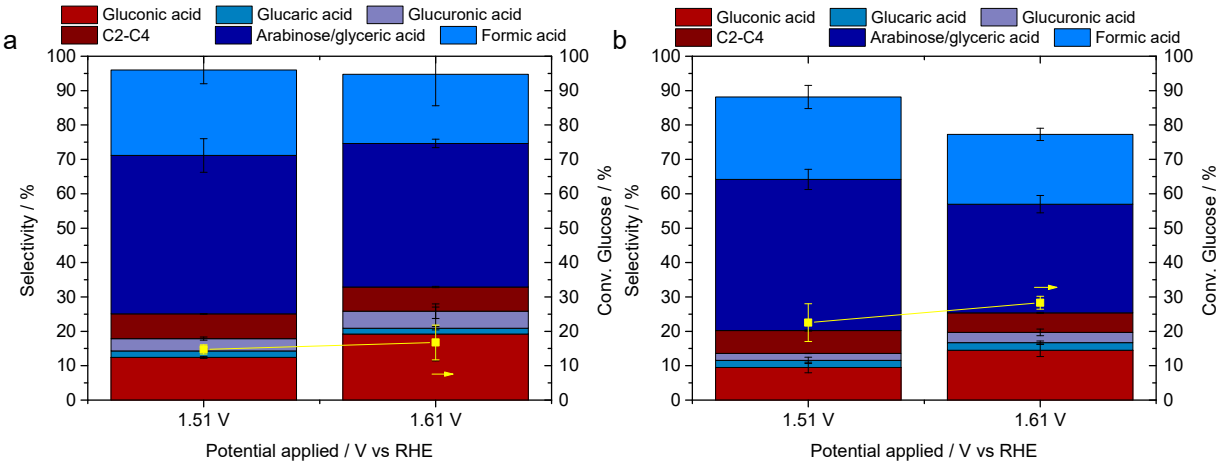


Figure S7. Glucose conversion, gluconic and glucaric acid and main by-products selectivity during the electrolysis of a glucose 0.05 M solution at 1.51 and 1.61 V vs RHE over NiO/Ni. Accumulated charge a) 50 C and b) 100 C.

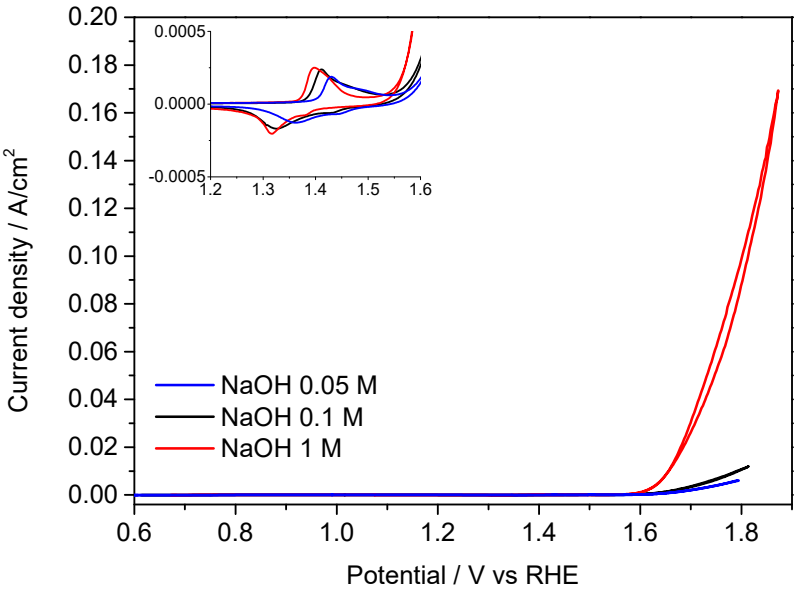


Figure S8. CVs recorded at the NiO/Ni foam in NaOH electrolytes of different concentration (0.05, 0.1 and 1 M). Conditions: 0.61 - 1.81 V vs RHE; scan rate 5 mV s^{-1}.

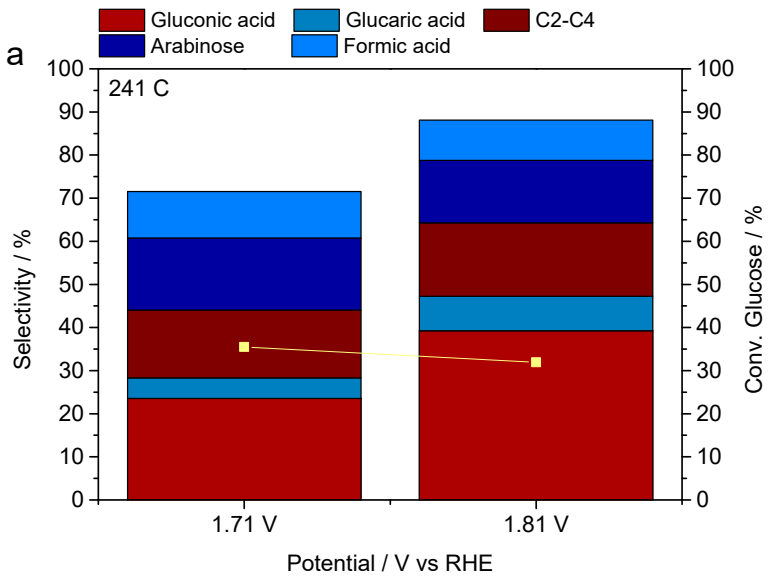


Figure S9. Glucose conversion, gluconic and glucaric acid and main by-products selectivity during the electrolysis of a glucose 0.05 M solution in NaOH 1 M at 1.71 and 1.81 V vs RHE over NiO/Ni. Accumulated charge 241 C.