Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary information

NiFeO$_x$

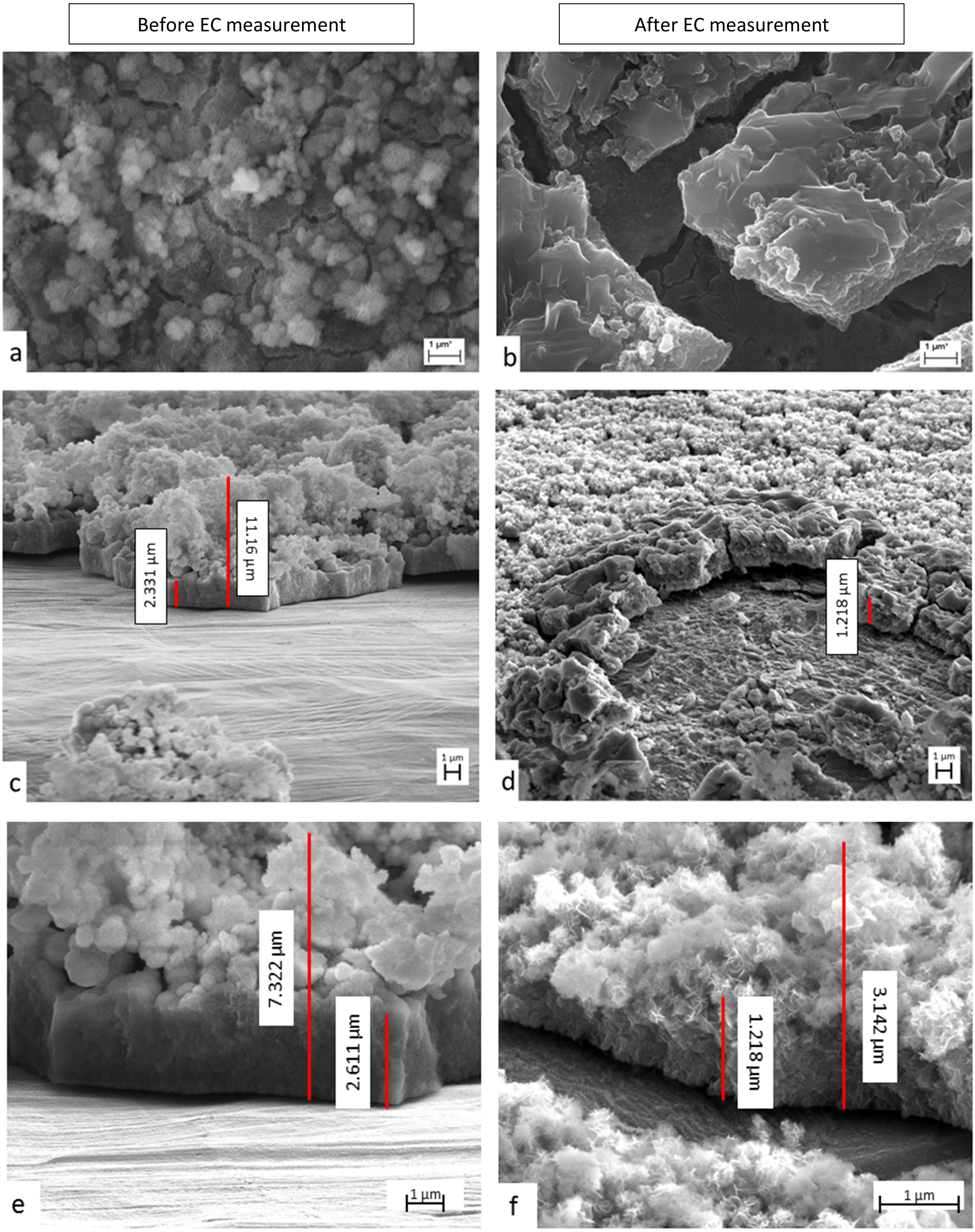

Figure S1: Scanning electron microscopy (SEM) images and cross section images of $NiFeO_X$ containing 20 mol% Fe, deposited for 40s at -10 mA/cm² in the pulsed deposition mode prior (a, c, e) and after (b, d, f) the electrochemical measurements. Comparing (a) and (b) shows that before the electrochemical measurements the surface consists of more cluster like structure, while after the measurements the surface appears to be flatter. After the measurements, more cracks appear and the cracks at different layers overlay each other. S1 (c) and (e) show the cross section before the electrochemical measurements and (d) and (f) show the cross section after electrochemical measurements. The height of the film tends to reduce after the measurements. Two different layer structures exist for the catalyst both before and after the electrochemical measurements. The first layers, which start to grow on the Ni substrate surface, appear to be denser compared to the top layers. The second layers, growing on the top, appear to be less dense and has more voids. Mostly the dense bottom layer exists after the measurements and less of the top layer can be observed.

NiMo

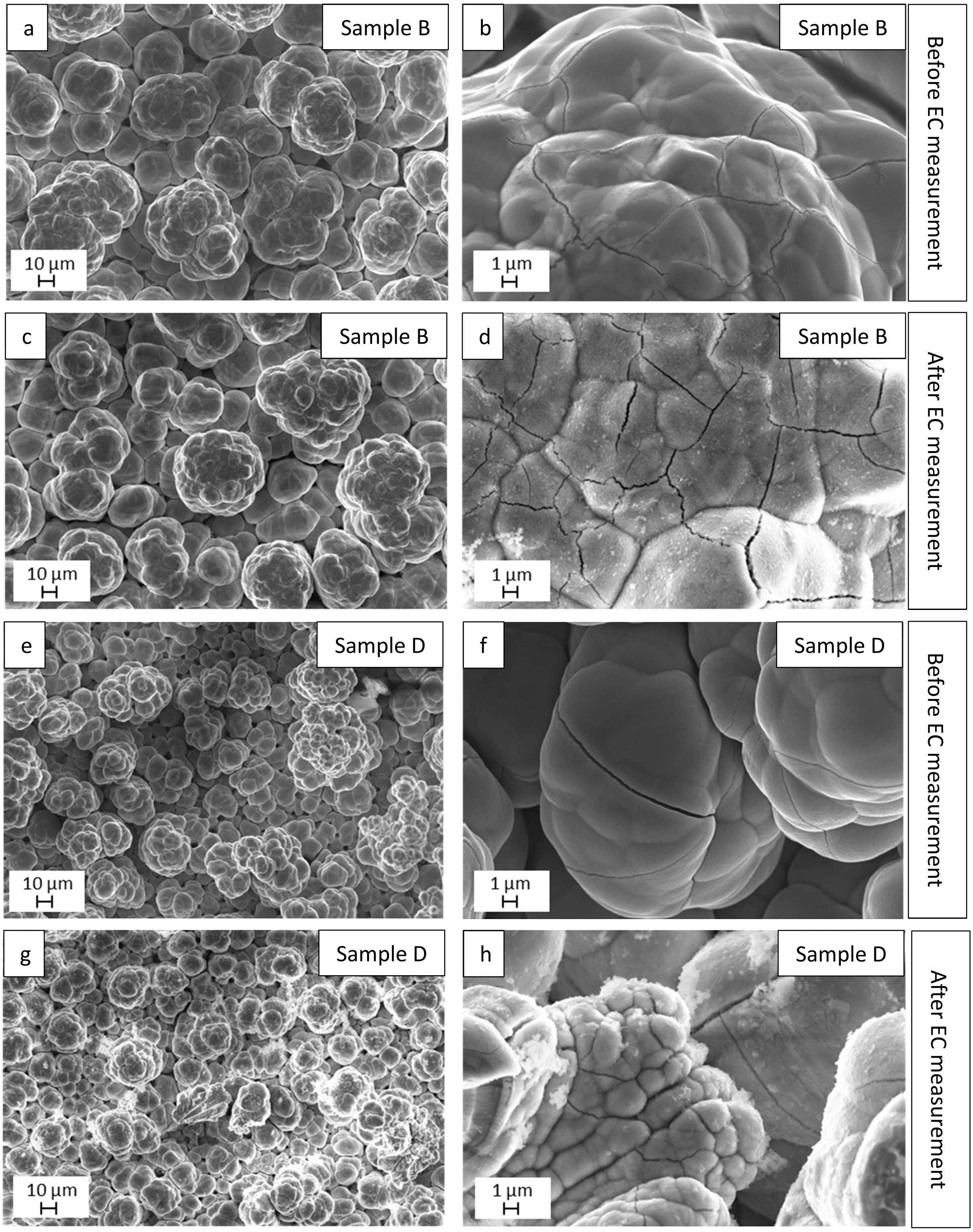

Figure S2: Scanning electron microscopy (SEM) images of NiMo samples B (a, b, c, d) and D (e, f, g, h) before (a+b, e+f) and after (c+d, g+h) the electrochemical measurements. Both samples were deposited under constant charge density conditions (Q_{dep} = -192 C/cm²) which results in the same surface morphology (compare a+b to e+f). The obtained surface morphology is well preserved after the electrochemical measurements (compare a+b to c+d and e+f to g+h). After the electrochemical measurements (c+d, g+h) small residues of dried electrolyte can be seen on the surface.

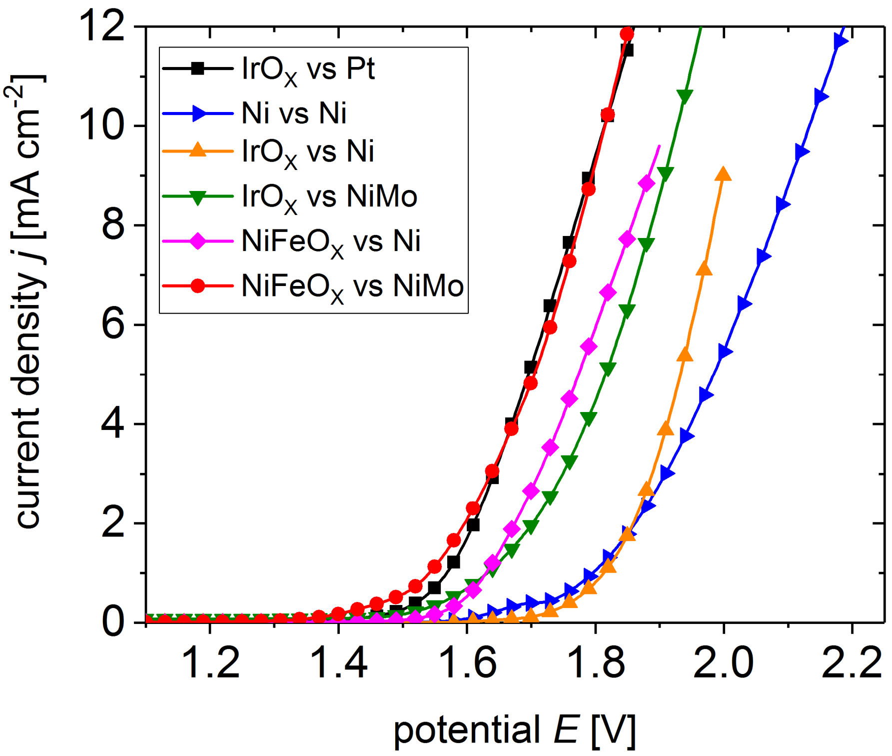

Figure S3: Linear sweep voltammetry curves of different catalyst systems on 50.3 cm² geometrical electrode area.

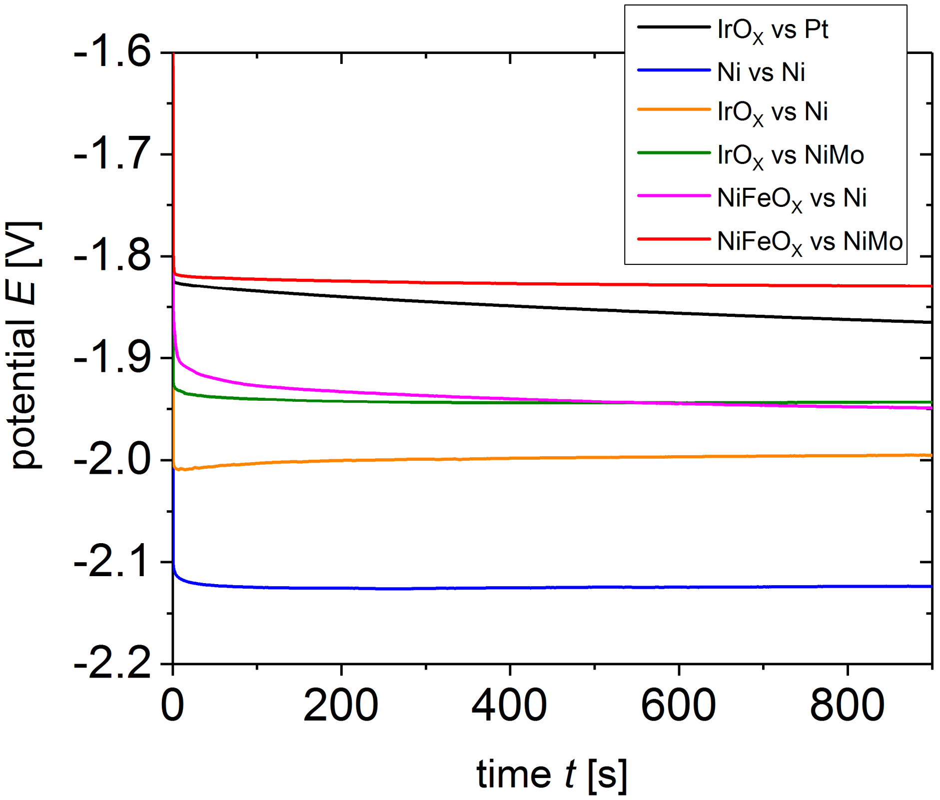

Figure S4: Chronopotentiometry scans for different catalyst systems on 50.3 cm² geometrical electrode area.

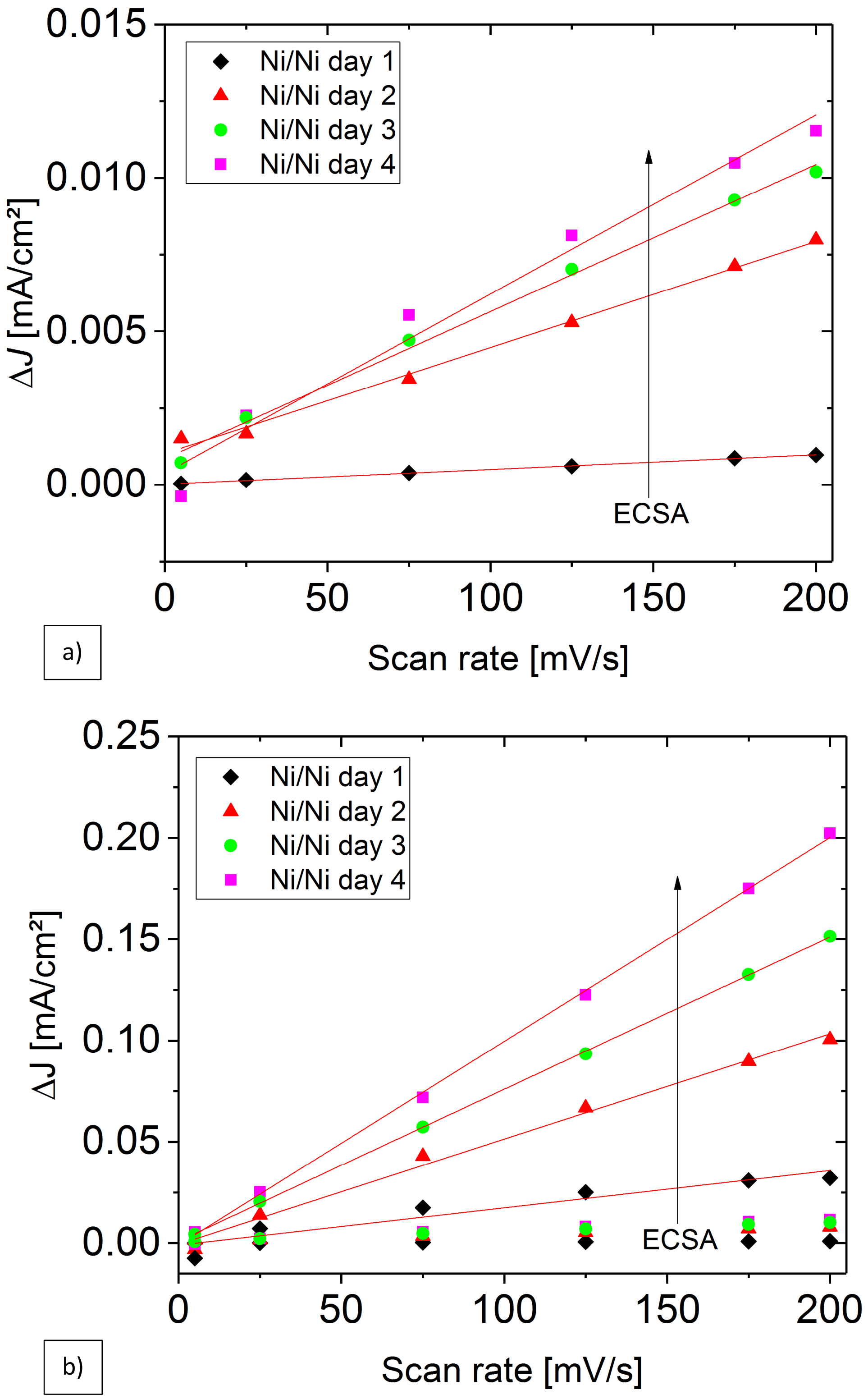

Figure S5: a) Δ*J* versus scan rate for determination of the electrochemically active surface area for Ni/Ni before the operation (black dots) and after the resting time, prior to the following operation hours (red, green, magenta signs). b) Δ*J* versus scan rate for determination of the electrochemically active surface area for Ni/Ni directly after the operation prior to the resting time. The increasing electrochemically active surface area is indicated and proportional to the slope.

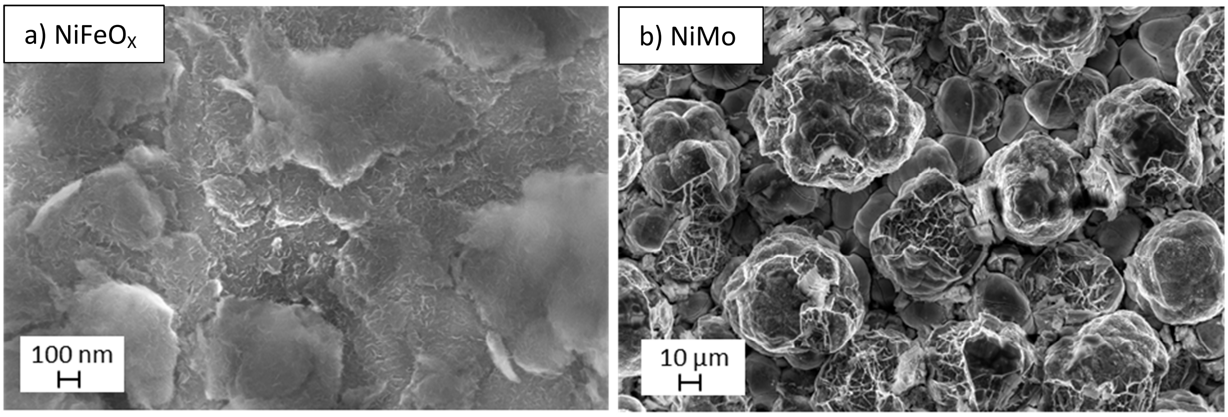

Figure S6: Scanning electron microscopy images of NiFeO$_X$ (a) and NiMo (b) after the measurement under simulated day-night-cycle conditions (6h of operation under 10 mA/cm², no bias over night). For NiFeO$_X$ (a) it can be seen that catalyst layers remain on the surface, although the size of the NiFeO$_X$ structures decreased compared to figure S1. In the case of NiMo (b), the surface morphology is similar compared to figure S2 (a, e).