Electronic Supplementary Material (ESI) for ChemComm.

From passivation to activation – Tunable nickel/nickel oxide for hydrogen evolution electrocatalysis

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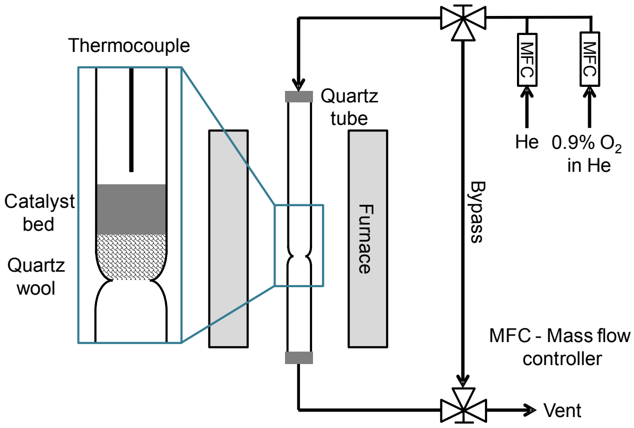
1. Experimental

1.1. Synthesis

For the preparation of the NiC composites, 1.4 g of nickel acetate tetrahydrate and 0.56 g of 2,5-dihydroxyterephthalic acid were dissolved in 37.5 mL water and 37.5 mL tetrahydrofuran (THF). After 15 min of stirring, the two solutions were mixed in a 100 mL Teflon-lined autoclave, which was sealed and subjected to a hydrothermal reaction at 383 K for 72 h. The resultant yellow powder was washed thoroughly with water and ethanol, and left to dry in air. The dried power was then placed in a crucible, and calcined at 773 K for 2 h, then at 973 K for 3 h in a tube furnace under an argon environment to afford NiC-0. The ramping rate for the calcination process was 3 K min^{-1}.



Scheme S1: Schematic of thermal oxidation rig utilised to controllably oxidise NiC composites

For the controllable oxidation, a system initially utilised for passivation, depicted in Figure S1, to oxidize samples under varying conditions. Typically, 100 mg of NiC-0 was loaded into a glass tube (300 mm long, 6 mm ID) atop a plug of quartz wool with a thermal couple being place in the reactor, directly above the bed. The sample was heated, at 1 K min^{-1}, under 40 mL min^{-1} of 0.5 % O_2 in He (Linde, 0.9 % O_2 in He, diluted by Coregas He, > 99.999 %) or in air (Coregas, dry air) to a fixed temperature and held for either 0.5 h or 2.0 h depending on the sample (as outlined in Table 1). The samples were subsequently cooled to room temperature under 40 mL min^{-1} He.

1.2. Physical and Chemical Characterization

XPS was performed on a Thermo ESCALAB250i X-ray Photoelectron Spectrometer. TEM was performed using a Philips CM 200 microscope. XRD was performed on a PANalytical X'Pert instrument. STEM was performed using a JEOL JEM-ARM200F microscope. TGA was carried out on a TA instruments TGA Q5000 with the sample being heated under air (Coregas, dry air) at 20 K min^{-1} to 1073 K.

1.3. Electrochemical Characterization

All electrochemical measurements were carried out with a CHI 750E electrochemical workstation (CH Instrument). The obtained NiC composites as well as the powdered Pt/C (20 wt% of Pt, Sigma-Aldrich) catalyst were prepared into inks before drop-casting onto the GC rotating disc electrodes (RDE). Specifically, 5mg of each sample powder was added into a 0.5 mL water and 0.5 mL ethanol mixture, followed by the addition of 25 μL of Nafion 117 solution (Sigma-Aldrich). The mixture was sonicated for 0.5 h to form homogeneous ink. Then, the catalyst inks were drop-casted onto the GC RDE to reach the same loading of 0.25 mg cm^{-2}. The polarization curves for HER were obtained with the catalyst coated GC RDE in 1 M PB solution (pH = 7) at 1600 rpm with iR corrections. A graphite rod was applied as the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode. All measured potentials were calibrated to RHE using the following equation: E_{RHE} (V) = E_{SCE} (V) + 0.245 + 0.059 ×pH. The scan rate for all electrodes is 5 mV s^{-1}. The chronoamperometric measurement was carried out in a customized electrolytic cell, using a piece of glass frit to separate the anode and the cathode. NiC composites drop-casted carbon fiber paper (CFP) with a loading of 0.5 mg cm^{-2} was employed as the working electrode, and a Pt wire was used as the counter electrode. The chronoamperometric measurement was performed without compensating the *iR* drop. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 100000 to 0.1 Hz at an applied overpotential of 150 mV.

2. Results

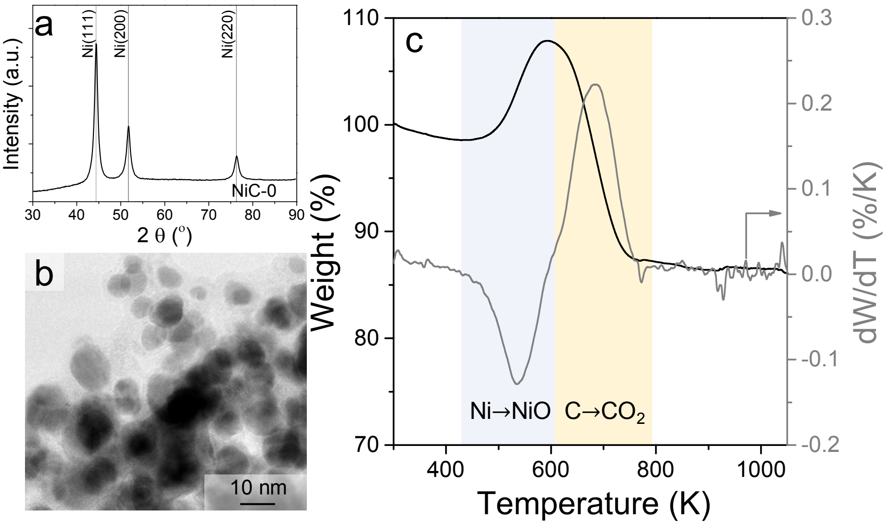


Figure S1. (a) XRD, (b) TEM and (c) thermogravimetric analysis (TGA) along with derivative weight (dW/dT) curves of the native NiC sample (NiC-0). Shaded regions indicate the zones of weight gain from Ni oxidation and weight loss from C gasification.

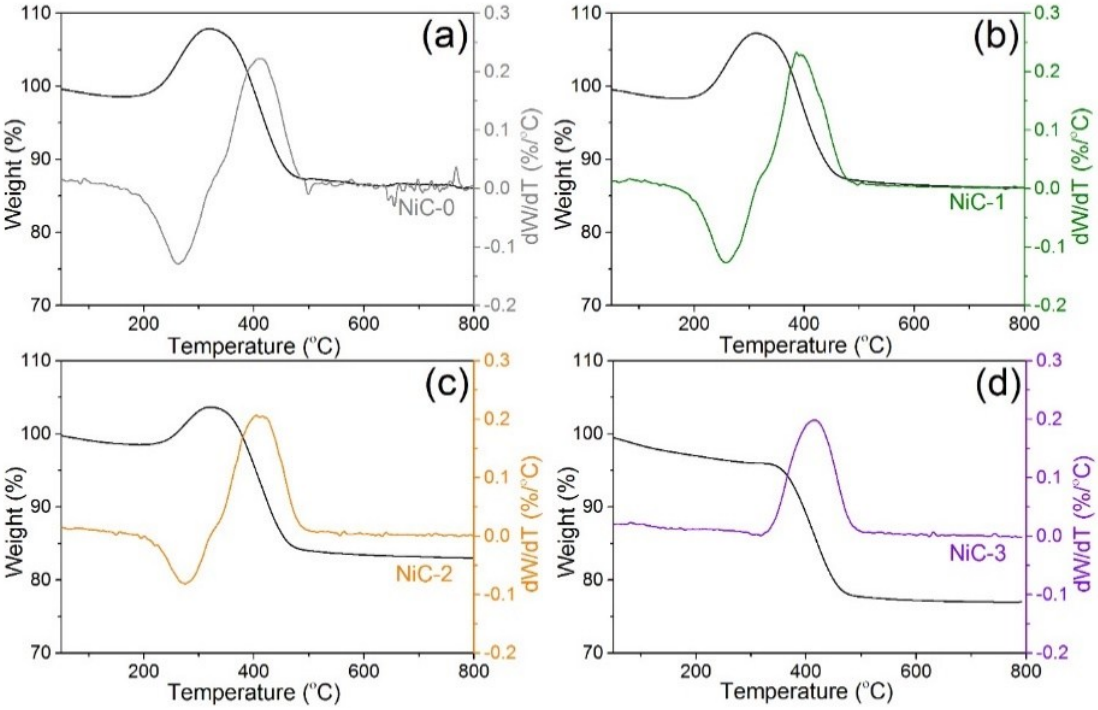


Figure S2. TGA of (a) NiC-0, (b) NiC-1, (c) NiC-2 and (d) NiC-3 composites with weight change and derivative weight (dW/dT) curves

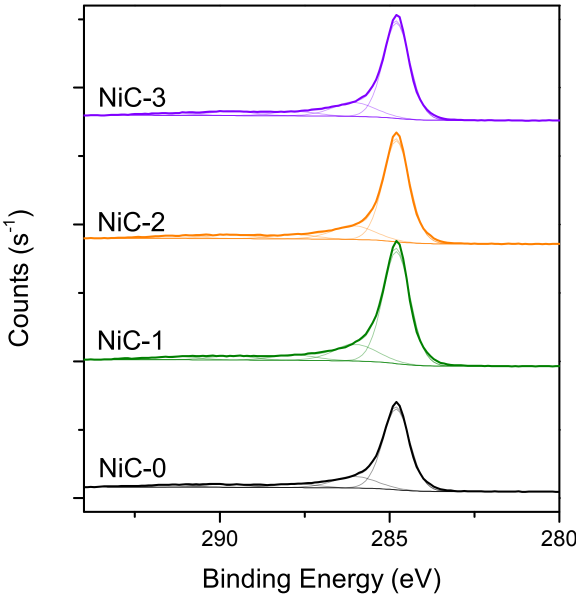


Figure S3. C1s XPS results of NiC samples with varying degrees of oxidation (NiC-0 to NiC-*3)*

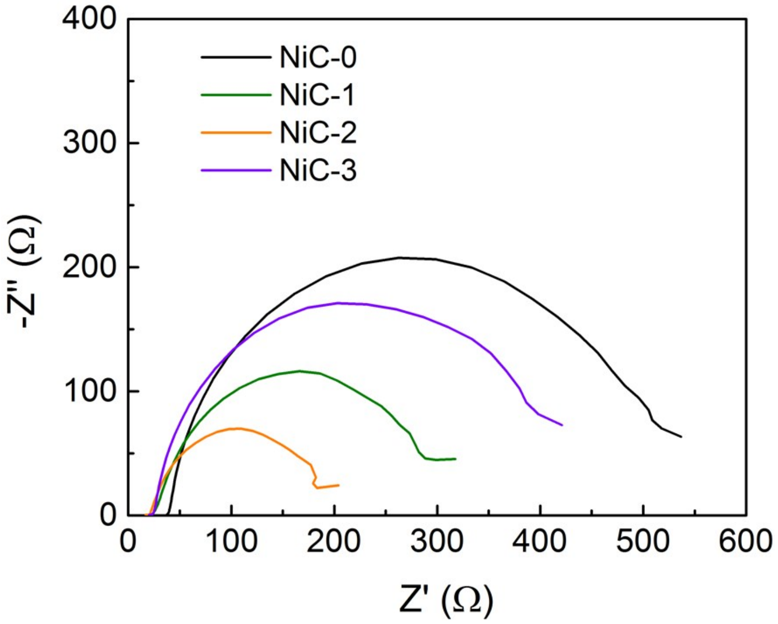


Figure S4. EIS spectra of the NiC composites obtained at 150 mV of applied overpotential in the 1 M PB solution.

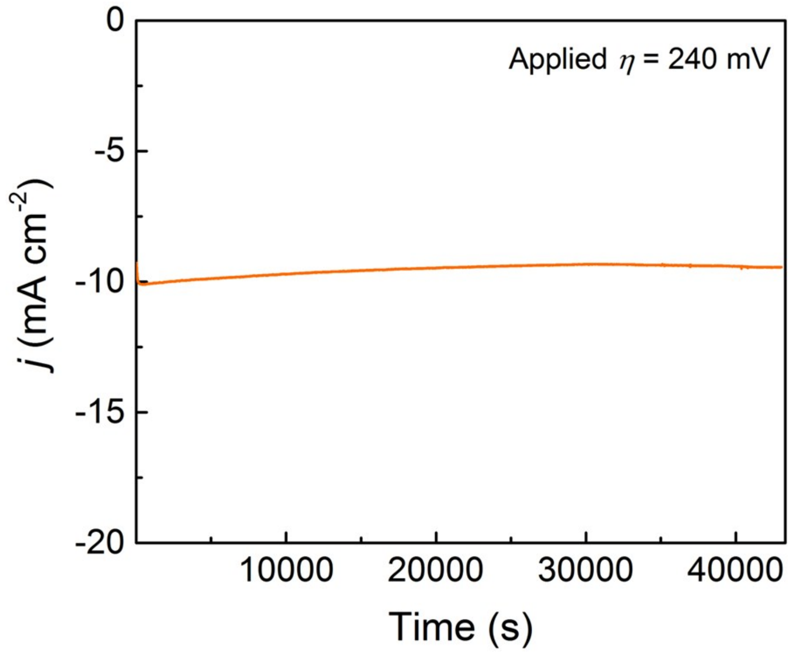


Figure S5. The chronoamperometric curve obtained with the NiC-2 drop-casted carbon fiber paper (loading = 0.5 mg cm^{-2}) in 1 M PB solution with a constant applied potential of -0.24 V. This test was carried out in a two-compartment electrolytic cell, where the anode and cathode was separated by a piece of glass frit. Pt wire was employed as the counter electrode.

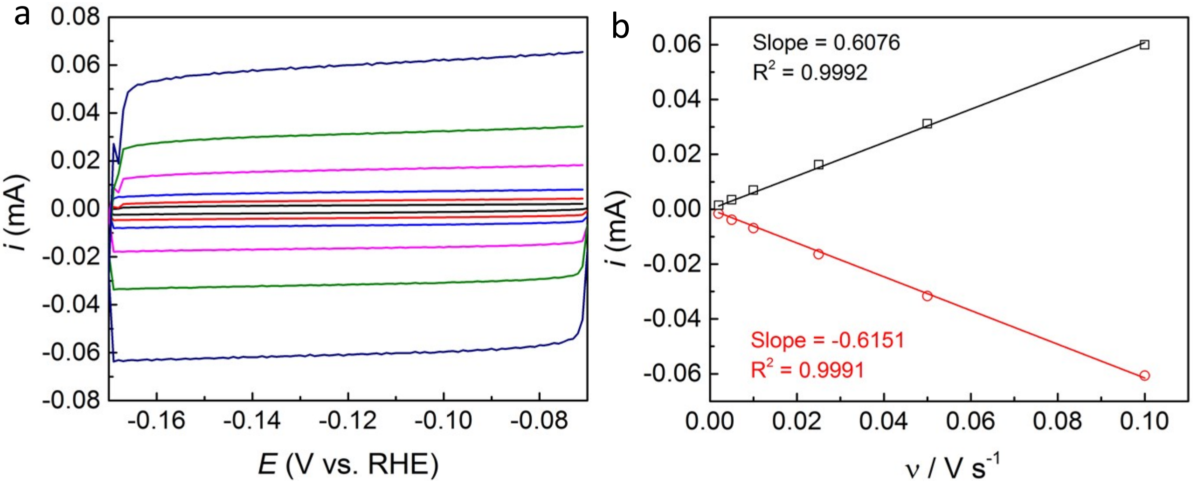


Figure S6. (a) Charging currents measured in the non-Faradaic potential range at scan rates of: 2, 5, 10, 25, 50 and 100 mV s^{-1} with the NiC-2 drop-casted GC electrode. (b) The cathodic (red circle) and anodic (black square) charging currents measured at -0.12 V vs. SCE with the NiC-2 drop-casted GC electrode, plotted against the scan rates. The double-layer capacitance determined herein is calculated by the average of the absolute value of anodic and cathodic slopes of the linear fits. The calculation of roughness factor (RF) can be referred to [1] and will not be described herein.

As shown in Figure S6, the roughness factor (RF) of NiC-0, NiC-1, NiC-2 and NiC-3 were 50, 70, 90, and 130, respectively.

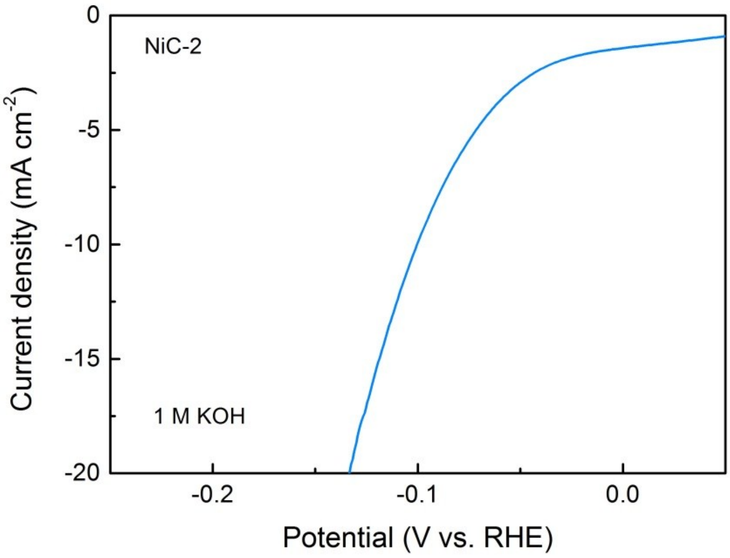


Figure S7. HER polarization curve obtained for the NiC-2 composite drop-casted glassy-carbon electrodes in 1 M KOH solution.

3. References

[1] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *Journal of the American Chemical Society* **2013**, *135*, 16977-16987.