Supplementary Information (SI) for ChemComm.

Electronic Supporting Information

Influence of Cation on Nitrate-to-Ammonia Synthesis over NiO:SnO_2: Insights from Differential Electrochemical Mass Spectrometry

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1. Methods

1.1 Material preparation

The NiO:SnO$_2$ NFs were prepared using NiCl$_2$•6H$_2$O (ACS grade, Sigma-Aldrich) and SnCl$_2$•2H2O (ACS grade, Sigma-Aldrich) as precursors. For the electrospinning solution, the Ni and Sn salts were dissolved in 100% technical-grade ethanol (BOOM B.V., The Netherlands). Next, polyvinylpyrrolidone (PVP, MW ~1,300,000, Sigma-Aldrich) was added to the solution, and the mixture was magnetically stirred overnight. The total concentration of metal ions in the solution was 0.063 M, with 25 mol% Ni and 75 mol% Sn, and 0.046 mM PVP.

A commercial electrospinning system from Vivolta (The Netherlands) was used to electrospin the fibers. For electrospinning the fibers, a potential of 10.25 kV, a stainless-steel needle with an inner diameter of 0.4 mm, a separation distance of 12 cm between the needle and the aluminum collector plate, and an infusion flow rate of 1.75 mL/h were used.

The nanofibers were collected at 22°C and a relative humidity of 30%. After deposition, the excess solvent was removed by keeping the nanofibers in a furnace at 80°C for 12 h.

To form the oxides, the collected fibers were annealed (Nabertherm LH 15/12) in air using two annealing steps. The first annealing step removes the organic components; the precursor fibers were annealed at 350°C (1°C/min) for 3 h. For the second step, calcination continued to 550°C (1°C/min) to generate NiO:SnO$_2$. No controlled cooling ramp was used.

1.2 Electrochemical experimental setup

Electrochemical measurements were performed using a potentiostat-galvanostat (VersaStat 3 from Princeton Applied Research) in a three-electrode configuration, which included a carbon rod as the counter electrode (CE), a reversible hydrogen electrode (RHE) employing 0.5 M H$_2$SO$_4$ as the reference electrode (RE), and a glassy carbon electrode (3 mm in diameter) as the working electrode (WE). A homogeneous catalyst dispersion was prepared by mixing 10 mg of catalyst with 1 mL of a water-isopropanol solution (3:1 volume ratio) and adding 70 µL of 5 wt.% Nafion, then ultrasonically mixing for thorough dispersion. Subsequently, 5 µL of this suspension was applied to the glassy carbon electrode and allowed to dry at room temperature, resulting in a loading mass of ca. 0.66 mg/cm^2. All tests were performed in 1 M of supporting electrolyte (LiOH, NaOH, and KOH) with 0.1 M of the corresponding nitrates (LiNO$_3$, NaNO$_3$, and KNO$_3$). Note that prior to all electrochemical measurements, the electrolyte was purged with Ar to eliminate dissolved oxygen, thereby suppressing the oxygen reduction reaction (ORR). Under the applied potential window investigated in this work, ORR is therefore considered negligible. Although ORR may become relevant at more positive potentials (typically between ~0.2 and 0.8 V vs. RHE), it does not contribute under the conditions employed here.

1.3 SEM

High-resolution (HR)-SEM morphological characterization was made by using a Zeiss MERLIN SEM microscope operated at 1.4 kV. A High-Efficiency Secondary Electron Detector (HE-SE2) was coupled to the microscope. The powder samples were analyzed by mounting them on top of conductive carbon tape.

1.4 STEM

Scanning transmission electron microscopy (STEM) characterization was performed using a JEOL ARM 200 CF microscope system operated at 80 kV. The estimated current density and the annular detector's inner and outer angles during imaging were 14.5 pA and 68-175 mrad. For the Transmission electron microscopy images, a Philips CM300ST-FEG Transmission Electron Microscope operated at 300 kV was used. The samples were prepared by sonicating 5 mg of the nanofiber powder suspension (in ethanol) for 5 min. After sonication, the suspension was drop-cast on Cu grids. The EDXS analysis was performed using a JEOL Centurio Energy-Dispersive X-ray spectrometer.

1.5 XRD

The structural characterization by X-ray powder diffraction was performed using a Bruker D2 PHASER diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) operated at 30 kV and 10 mA. X-ray spectra were taken in the 2θ range of 20-90°, using a step size of 0.05° and a scan speed of 0.1°/s. Powder samples were supported in a Si low-background sample holder (Bruker).

1.6 DEMS

An electrochemical micro-reactor using a three-electrode configuration was used to record the ionic and faradaic currents as a function of electrode potential (and time). The electrochemical measurements were performed using a potentiostat-galvanostat (µAutolab III). The cell was coupled in line with a mass spectrometer (DEMS) equipped with a quadrupole mass spectrometer (Prisma QMG220) at a working pressure of approximately 2.7×10^{-5} mbar. The mass signal (hereafter ionic current) for selected mass-to-charge ratios (m/z) and the current-potential profiles were recorded simultaneously at a scan rate of 1 mV/s. All solutions were saturated with Ar before the DEMS analysis.

1.7 EIS

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Electrochemical impedance spectroscopy (EIS) was used to study charge transport processes at the electrode-electrolyte interface using steady-state techniques. This analysis utilized a sinusoidal signal of 10 mV amplitude in the frequency range from 100,000 to 0.1 Hz at an applied potential of -0.25 V vs. SHE in the different electrolyte solutions. All experiments were performed at room temperature, and the solutions were saturated with Ar for 15 minutes before the experiments.

2 STEM-EDX

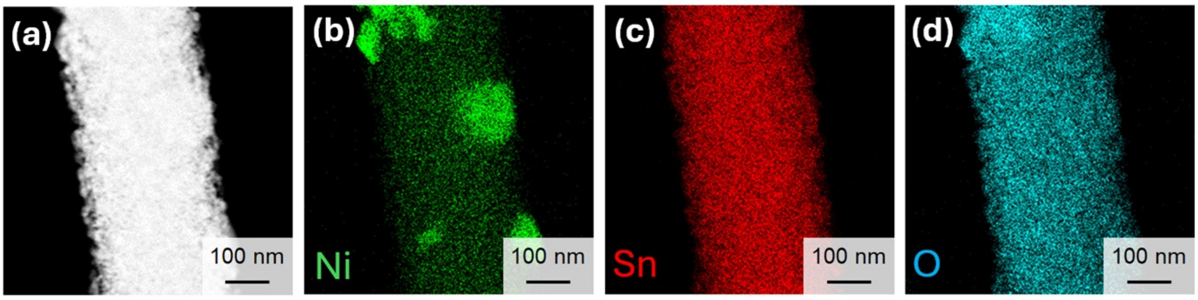

Figure S1. (a) dark-field STEM, and (b-d) STEM-EDX maps for NiO:SnO_2 NF.

3 Product distribution relationship

Table S1. Relationship values of NH_3/H_2 in the various electrolytes at different applied potentials

Potential	NH_3/H_2 relationship values		
	KOH	NaOH	LiOH
-0.25 V	0.846	5.600	0.877
-0.35 V	0.253	1.987	1.479
-0.45 V	0.109	2.099	0.381

4 EIS and proposed mechanism

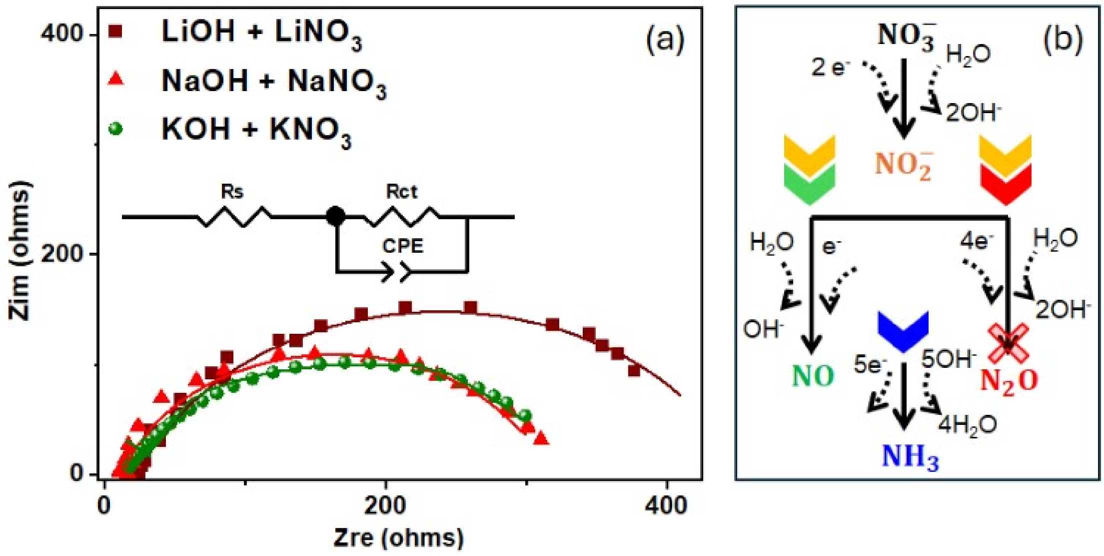

Figure S2. (a) Nyquist plots for NiO:SnO$_2$ NFs in KNO$_3$ with KOH, NaNO$_3$ with NaOH, and LiNO$_3$ with LiOH measured at -2 mA/cm^2. (b) A proposed NO$_3$-RR mechanism mediated by the electrolyte is shown at a bias potential of -0.25 V vs RHE.

Table S2. *Electric parameters for NiO:SnO$_2$ NF*

Element	**KNO$_3$+KOH**	**NaNO$_3$+NaOH**	**LiNO$_3$+LiOH**
Rs	20.87	19.77	22.79
Rct	270.3	335.8	430
CPE-T	0.000283	0.000158	0.000146
CPE-P	0.697	0.816	0.769