Supporting Information

From RRDE to GDE: Loading-Dependent H_2O_2 Selectivity Loss in Sn- and Sb-N-C Catalysts

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S1 Materials and synthesis

S1.1 Chemicals

$SnCl_2 \cdot 2H_2O$ (ACS, 98.0-103% - Thermo Scientific Chemicals), 1,10-phenantroline (ACS - Alfa Aesar), $TiOSO_4 \cdot xH_2O$ (≥ 29% Ti (as TiO_2) - Riedel-de Haën), MilliQ water (18.2 MΩ), Nafion (perfluorinated resin 5% w/w lower aliphatic alcohols and water - Sigma Aldrich), acetone (HPLC > 99.9% - VWR Chemicals), H_2O_2 (30% w/w - Sigma Aldrich), KOH (≥ 85% - Sigma Aldrich), K_2SO_4 (ReagentPlus, ≥ 99% - Sigma Aldrich), H_2SO_4 (Emsure, 98% - Supelco), Vulcan XC-72 carbon (Fuel Cell store).

S1.2 $Sn(phen)Cl_2$ complex synthesis

Starting compounds, namely $SnCl_2 \cdot 2H_2O$ and 1,10-phenantroline, were solubilized in ethanol or isopropanol in two distinct vessels in a ratio of 1:2 $Sn^{II}Cl_2$:phenantroline. Next, the solutions were combined, resulting in the immediate formation of a yellow precipitate. The precipitate was then filtered with a Büchner funnel and washed with ice-cold ethanol within 10 minutes of its formation in order to avoid degradation of the product. The compound was then dried in a vacuum oven at 40°C overnight.

S1.3 $Sb(phen)Cl_3$ complex synthesis

The procedure for $Sb(phen)Cl_3$ synthesis is analogous to that of $Sn(phen)Cl_2$, with the difference that $Sb^{III}Cl_3$ replaces $Sn^{II}Cl_2$.

S1.4 Sn-N-C synthesis

The following procedure has been used for the Sn-N-C catalyst: 100 mg of commercial carbon support, namely Vulcan XC-72, and 128 mg of $Sn(phen)Cl_2$ complex, equivalent to 4% molar respect to carbon, were mixed with the use of a quartz mortar. The homogeneous compound obtained from mixing was then put into a quartz vessel used for synthesis and then into a tubular oven. Then it was pyrolyzed at 900 °C for 2 h in an inert N_2 atmosphere. After that, the pyrolysis product was cooled at room temperature. Once cooled down, it was then ground with a mortar and refluxed in H_2SO_4 1 M at 100 °C for 3 hours under magnetic stirring. Then, the compound was filtered with a Büchner funnel and washed with water. Finally, it is dried in a vacuum oven and ground one last time with a mortar.

S1.5 Sb-N-C synthesis

The synthesis of the Sb-N-C catalyst is performed with a similar procedure to the one used for Sn-N-C. The main difference is the use of $Sb(phen)Cl_3$ as a metal complex.

S2 Experimental section

S2.1 RRDE electrodes preparation

Before each measurement, the GC-Pt electrode was cleaned. The cleaning procedure used involves rubbing the electrode surface with diamond pastes of increasingly finer grain size on special cloths: a first pass on a silk cloth with a 3 µm paste, a subsequent pass on the same cloth with a 1 µm paste, and a final pass on a velvet cloth with a 0.25 µm paste; each pass is interspersed with a wash with pure acetone in an ultrasonic bath for at least 5 minutes to completely remove any residue. The ink is prepared with an appropriate amount of catalyst, MilliQ water, and THF in a 70:30 proportion, and finally Nafion (a perfluorinated polyelectrolyte in a 5% w/w hydroalcoholic solution) in an amount such that $m_{cat}/m_{Nafion} \approx 1$. The ink is sonicated for at least 30 minutes to obtain a homogeneous suspension. The ink was then immediately deposited by dropcasting using a micropipette to reach a loading of 0.6 mg cm^{-2}.

S2.2 RRDE measurements

The electrochemical cell was filled with 0.1M KOH + 0.1M K_2SO_4 solution. Then a graphite rod was inserted serving as the counter electrode, a Hg/HgO electrode as reference, and the RRDE tip as the working electrode. The cell jacket is connected to a thermostat, which circulates water at a temperature of 25 °C. Once all electrical and gas connections have been made, Ar is bubbled through the solution for 30 minutes to remove all dissolved O_2. After the 30 minutes have elapsed, the bubbler valve is turned so that the gas flows into the cell without bubbling through the solution, and the measurement is started. The ohmic drop of the solution is then determined with an EIS measurement. Once the potential window of interest has been selected, a set of initial activation cycles (ca. 50) is performed at a scan rate of 200 mV s^{-1} until a constant overlap of the CV traces is obtained. This procedure allows the electrode to become fully wetted and removes any air or gas bubbles present on its surface, thereby ensuring the best possible contact with the electrolyte solution and consequently the best electrical conductivity. After activation, an LSV measurement (1600 rpm) of the

blank (Ar-saturated solution) is carried out in the cathodic direction, i.e., toward more negative potentials, at a scan rate of 5 mV s^{-1}, while maintaining the metallic ring of the RRDE electrode at a potential of 1.5 V vs. RHE. Once all the blank measurements have been obtained, the actual measurements are carried out: O_2 is bubbled into the solution for ca. 20 minutes, another EIS measurement is performed to determine the appropriate compensation value, and the same procedure used for the blanks is followed. For each catalyst, at least three measurements are performed using different electrodes. The cell was connected to a PARSTAT 3000A-DX.

S2.3 GDE electrodes preparation

GDE electrodes were prepared with vacuum deposition. A disk of Freudenberg H23C8 was covered with a catalyst + binder layer in the form of an ink. This was made by weighing the catalyst in a vial first, then adding a solvent (acetone in this case) and the binder (Nafion 5% solution) to it with a m_{cat}:$m_{binder\ sol.}$ ratio of circa 1:3. The ink is then sonicated for 30 minutes and then deposited on the carbon paper using the vacuum filtration setup. This setup uses a Millicup™-FLEX funnel and membrane support threaded on a GL45 glass bottle attached to a vacuum pump.

S2.4 GDE H-cell assembly

The experiments were set up as follows: a glass H-cell (as drawn in Fig.2, main text) was assembled by connecting the two compartments while keeping them separated using a Nafion membrane (25 µm, NR211, Chemours) and then connecting the gas supply apparatus to the cathodic compartment where the GDE is placed. The active area of the working electrode (WE)/catalyst with this setup is 1.66 cm^2. Subsequently, the compartments are filled with their respective solutions: 150 mL of 0.1 M K_2SO_4 and 0.1 M KOH (pH 13) solution for the cathodic compartment and 150 mL of 0.1 M K_2SO_4 and 0.05 M H_2SO_4 (pH 1) solution for the anodic compartment. The acidic solution (pH 1) in the anodic compartment is used to provide a greater gradient of proton concentration between the two compartments to speed up the migration process through the membrane. Hg/HgO was used as the reference electrode, and a carbon cloth as the counter electrode. The cell was connected to a PARSTAT 3000A-DX.

S2.5 H_2O_2 production experiments: experimental procedure

The same electrochemical procedure is performed in every H_2O_2 production experiment. At first, an activation is conducted, made up of 50 cyclic voltammetry (CV) cycles at a 100 mV s^{-1} scanning rate. Then, to have information on the initial state of the catalyst, a CV is performed using a scanning rate of 50 mV s^{-1}. After that, the sample is put through a 4-hour-long chronopotentiometry, with an applied current density of j = −5 mA cm^{-2} (−8.29 mA for the 1.66 cm^2 WE). To evaluate peroxide production, a volume of 0.5 mL is drawn every 30 minutes and analysed via UV-VIS spectroscopy to evaluate peroxide concentration. After 4 hours, a final CV is performed on the sample.

S2.6 H_2O_2 quantification

Peroxide quantification is performed via complexation of H_2O_2 with Titanium(IV) oxysulfate ($TiOSO_4 \cdot xH_2O$) to form a coloured compound visible with UV-VIS spectroscopy. By reacting with hydrogen peroxide, Ti^{IV} gives dihydroxoperoxo-species that can be detected via UV-VIS (peak of adsorption at 409 nm):

$$H_2O_2 + (TiO)^{2+} + H_2O \rightarrow Ti(O_2)(OH)_2 + 2H^+$$

The complexation solution is obtained as follows: a 0.02 M standard solution of Ti^{IV} is prepared in a 100 mL volumetric flask by mixing the right amount of Ti salt with 30 mL of milliQ water and 27.2 mL of H_2SO_4 until complete dissolution, and then adding water to reach the full volume. 0.5 mL of electrolyte is mixed with 1mL of Ti solution and brought to 2 mL with water. Calibration curve intercept and angular coefficient used for the following experiments are:

$$Abs_{409nm} = 0.03627 + 0.75325 * [H_2O_2]$$

S2.7 Mathematical formulas used

With H_2O_2 quantification, faradaic efficiency (FE%) can be obtained using the following formula:

$$FE\% = 100\frac{Q_{H_2O_2}}{Q_{tot}} = 100\frac{n_{H_2O_2}zF}{Q_{tot}}$$

where Q_{H2O2} is the effective charge used to produce H_2O_2, Q_{tot} is the total charge, n_{H2O2} is the number of H_2O_2 moles produced, z is the number of electrons needed to obtain a molecule of peroxide (2 in this case), and F is the Faraday constant.

To further evaluate the feasibility of H_2O_2 production with the catalyst used, energy consumption (electrochemical work) data is extrapolated from production experiments using the following formula:

$$W_{el} = \frac{\eta \cdot I}{\dot{n}_t}$$

where η is the overpotential (mediated over the 4h reaction time), I is the current passing at the WE, and $\dot{n}_t$ is the hourly production of H_2O_2. The performance of the catalyst is evaluated using J mmol^{-1} as a unit of measurement, where lower values indicate better catalytic activity.

This parameter could be directly linked to faradic efficiency (FE) as follows:

$$W_{el} = \frac{\eta \cdot I}{\dot{n}_t} = \frac{\eta \cdot I}{\frac{n_{H_2O_2}}{t_{tot}}} = \frac{\eta \cdot I \cdot t_{tot}}{n_{H_2O_2}} = \frac{\eta \cdot Q_{tot}}{n_{H_2O_2}} = \frac{\eta \cdot Q_{tot}}{\frac{Q_{H_2O_2}}{F \cdot n_{e^-}}} = \frac{\eta \cdot F \cdot n_{e^-} \cdot Q_{tot}}{Q_{H_2O_2}} = \frac{\eta \cdot F \cdot n_{e^-}}{FE}$$

All potential was converted against RHE using a commercial electrode (Gaskatel):

$$E_{RHE} = E_{Hg/HgO} + 1.038\ V$$

S2 Supporting Image

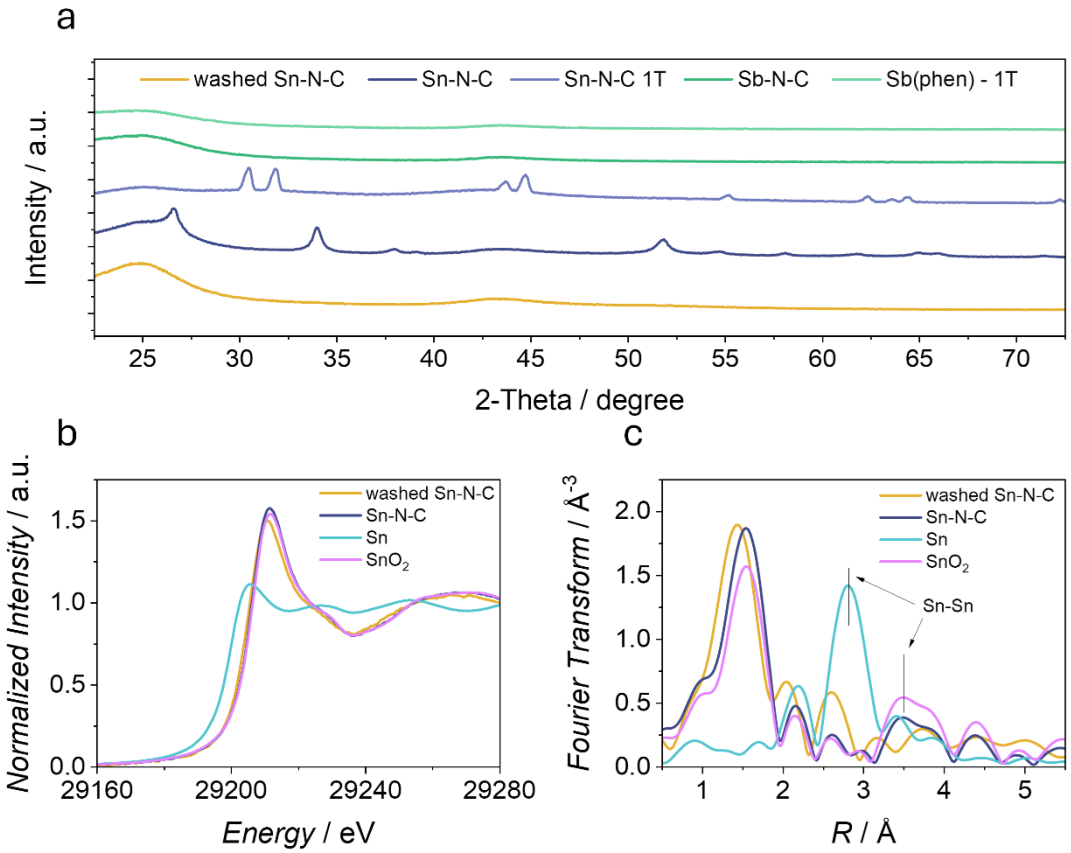

Fig. S1 a) Comparison of XRD profiles between catalysts before (1T) and after the acid leaching step. b, c) XANES and EXAFS profiles of Sn, SnO_2 standards, and Sn-N-C used in this paper, and a comparison with a similar synthesis with extensive acid washing to show the copresence of SnN_x sites and SnO_2 in the prepared Sn-N-C.

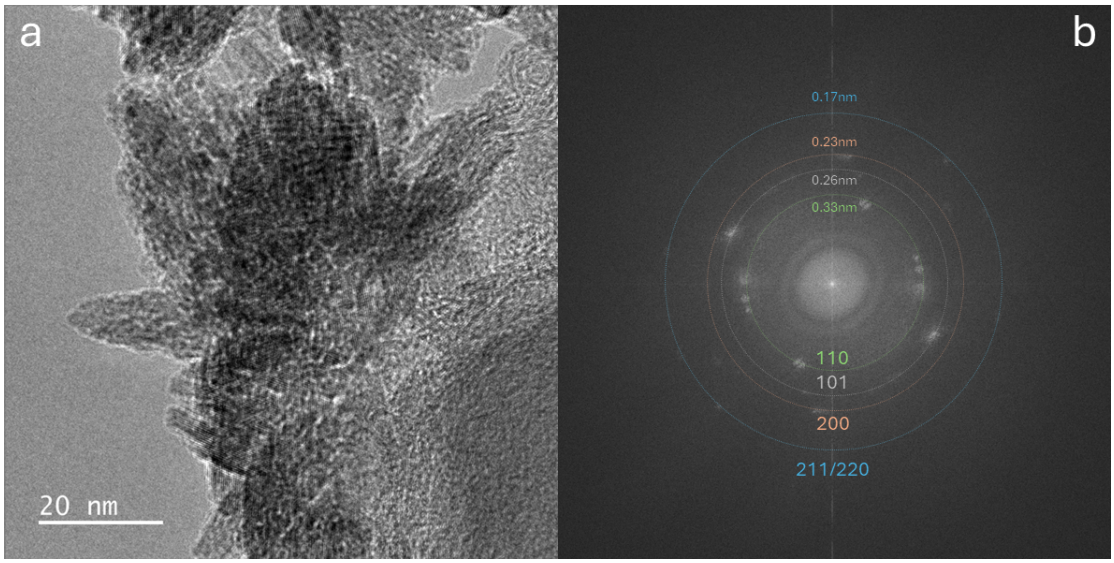

Fig. S2 a) TEM image of an agglomerate of SnO_2 nanoparticles in Sn-N-C, and b) the corresponding Fourier transform image, where peaks corresponding to the main crystallographic plane of tin oxide are visible. With different colors, the identification and plane distance are reported.

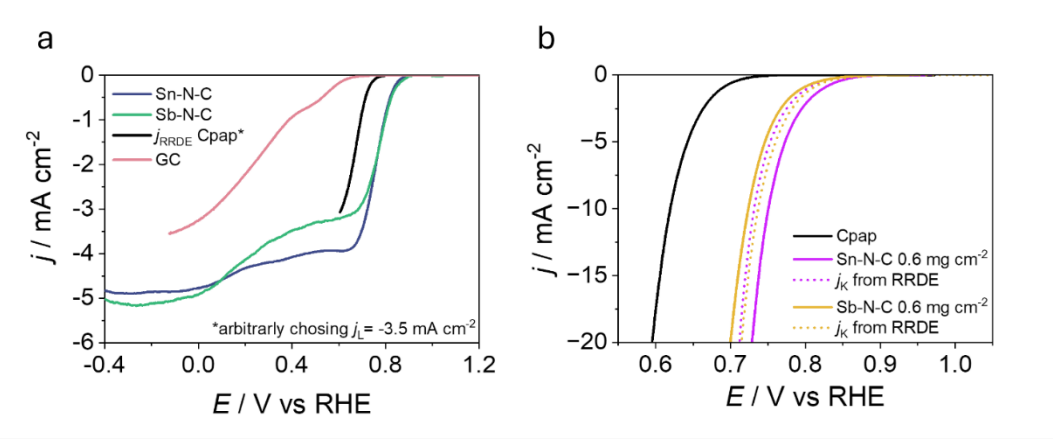

Fig. S3 a) Comparison between catalysts and "blank" support. In detail, GC is the measurement of the bare glassy carbon of RRDE, while the curve of carbon paper (Cpap) was extrapolated from the GDE measurement using the Koutecký–Levich equation and assuming a limiting current of −3.5 mA cm^{-2} arbitrarily; this does not change the profile in the kinetic region, and allows an easier comparison between RRDE and GDE. b) Similarly, an analogous comparison is made for GDE measurements. In this case, the pure kinetic current is calculated from RRDE measurements for the two catalysts, again using the Koutecký–Levich equation, and taking the first step limiting current (in the region around 0.5 V vs. RHE)

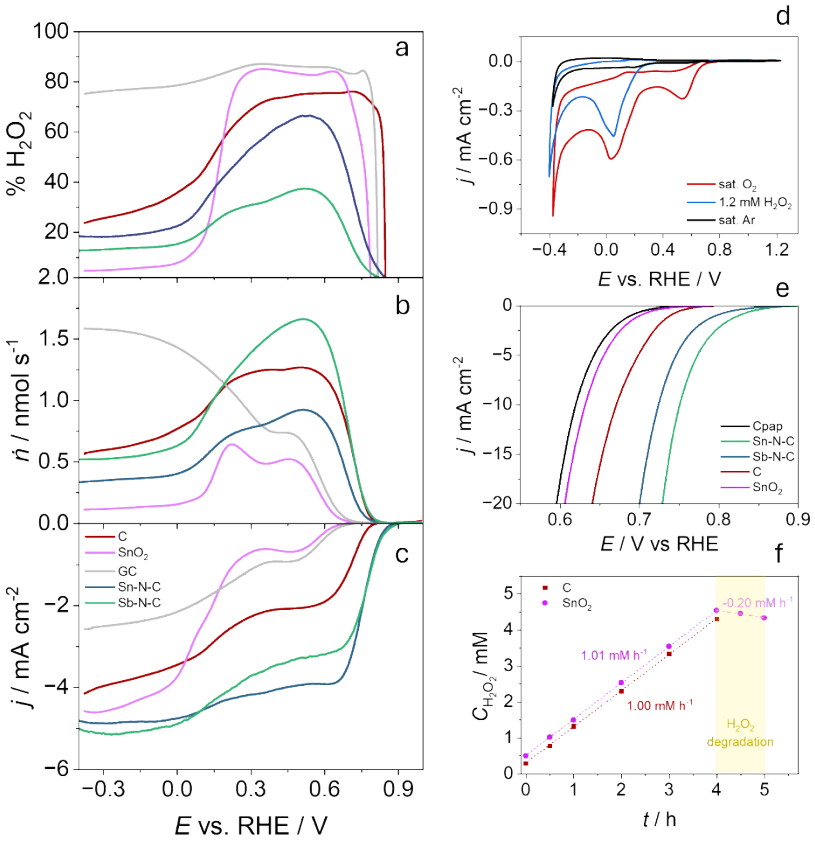

Fig. S4 a-c) RRDE results for the two catalysts, carbon support, bare GC, and sole SnO_2. Loading is 0.6 mg cm^{-2} for all measurements. d) Cyclic voltammetry in Ar and O_2-saturated electrolyte and in the presence of 1.2 mM of H_2O_2 (without oxygen) for SnO_2 . Scan rate 20 mV s^{-1}. e) Similarly, an analogous comparison for various materials is made for GDE measurements. f) Accumulation of H_2O_2 during GDE experiment with C and SnO_2 at -5mA cm^{-2}, loading 0.6 mg cm^{-2}. The last hour was made to prove that H_2O_2 is not significantly consumed by SnO_2.