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

Supporting Information

From Brew to Clean Fuel: Harnessing Distillery Wastewater for Electrolysis H_2 Generation Using Nano Scale Nickle Selenide Water Oxidation Catalysts

Michael Walsh,[a] Jeannie Z. Y. Tan,[a] Sanjay Nagarajan,[b] Kenneth Macgregor,[c] John M. Andresen,[a] M. Mercedes Maroto-Valer,[a] and Sudhagar Pitchaimuthu[a]*

a. Research Centre for Carbon Solutions (RCCS), Institute of Mechanical, Processing and Energy Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, United Kingdom.

b. Department of Chemical Engineering, University of Bath, Bath BA27AY, U.K. Address here.

c. The Scotch Whisky Research Institute, The Robertson Trust Building, Research Avenue North, Riccarton, Edinburgh, EH14 4AP, United Kingdom.

Corresponding author: E-mail: S.Pitchaimuthu@hw.ac.uk

S1. Surface morphology:

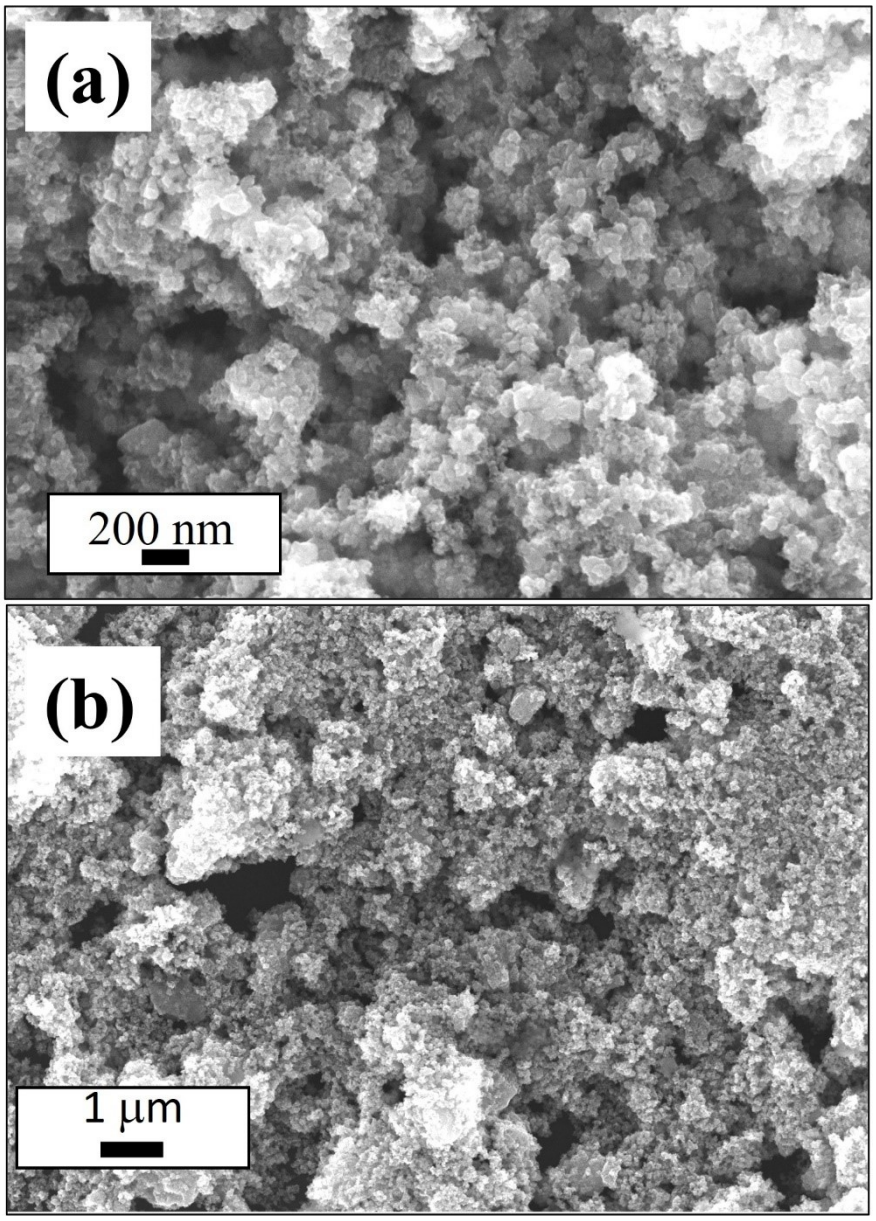

Figure S1. SEM of Ni_2Se_3 powder at (a) 200 nm scale and (b) 1 micron scale.

S2. NMR analysis:

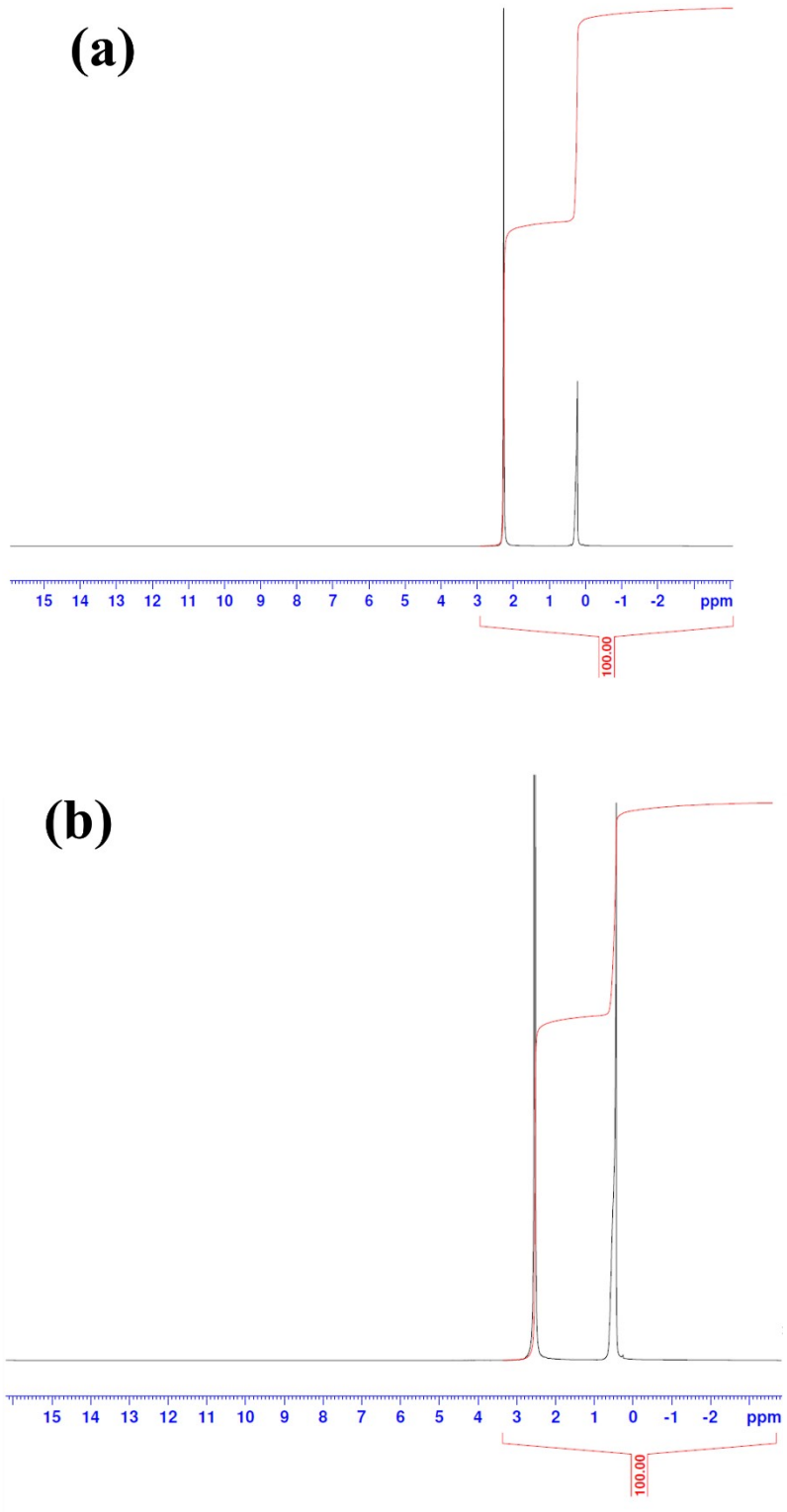

Figure S2. NMR spectra of distillery wastewater before and after electrolysis process.

S3. Diffusion co-efficient analysis:

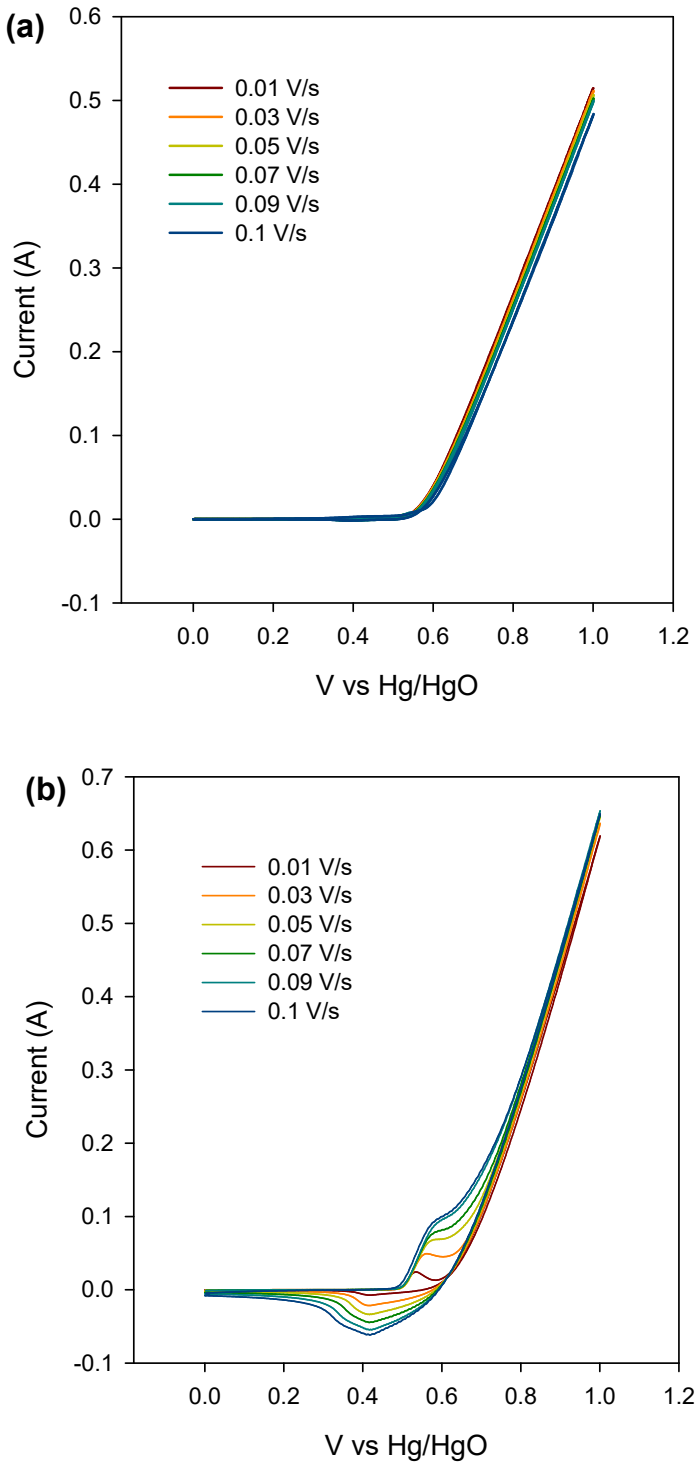

Figure S3. Cyclic voltammogram (CV) of Ni_2Se_3/SS anode in (a) freshwater and (b) distillery wastewater-based electrolyte measured at different scan rate (V/s). Note that the concentration of the electrolytes was 1.0 M NaOH.

S4. Compare with commercial water oxidation catalyst:

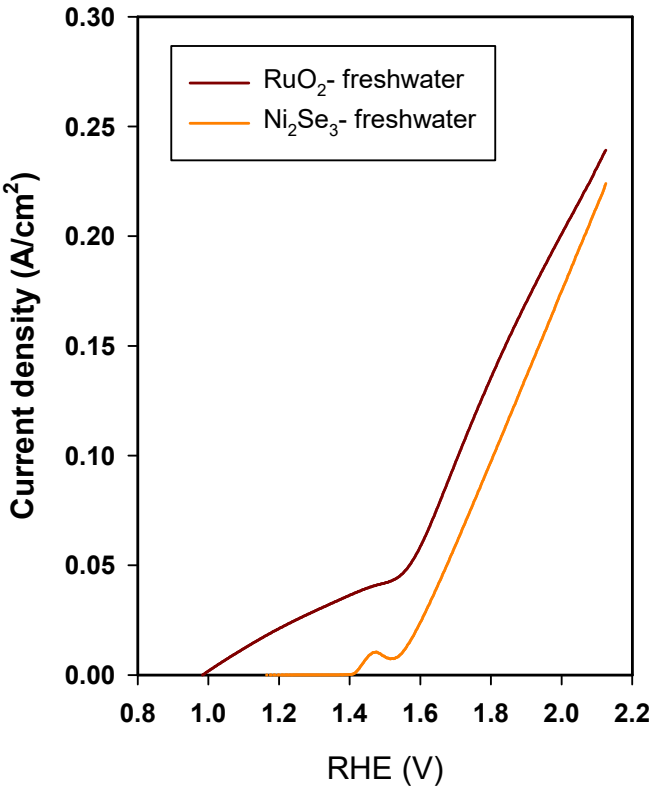

Figure S4. LSV plots of Ni_2Se_3/SS and commercial RuO_2 anode in freshwater-based electrolyte. Note that the concentration of the electrolytes was 1.0 M NaOH.

S5. Influence of organic substances present in the distillery wastewater feedstock

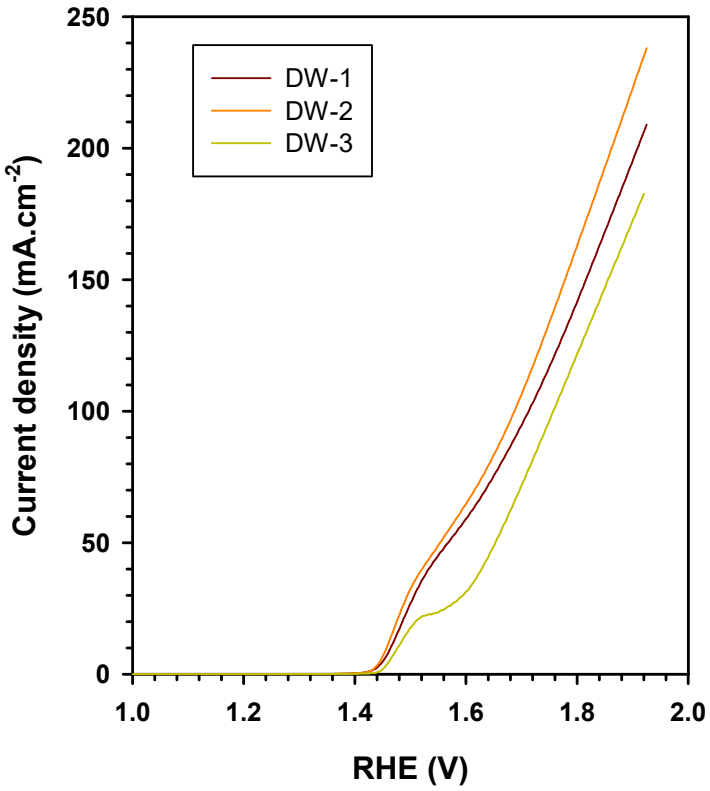

Figure S5: LSV Plots of Ni_2Se_3/SS in various distillery wastewater (DW) samples. The samples were collected at different processing stages and exhibit varying concentrations of organic substances.

S6. Oxygen evolution analysis:

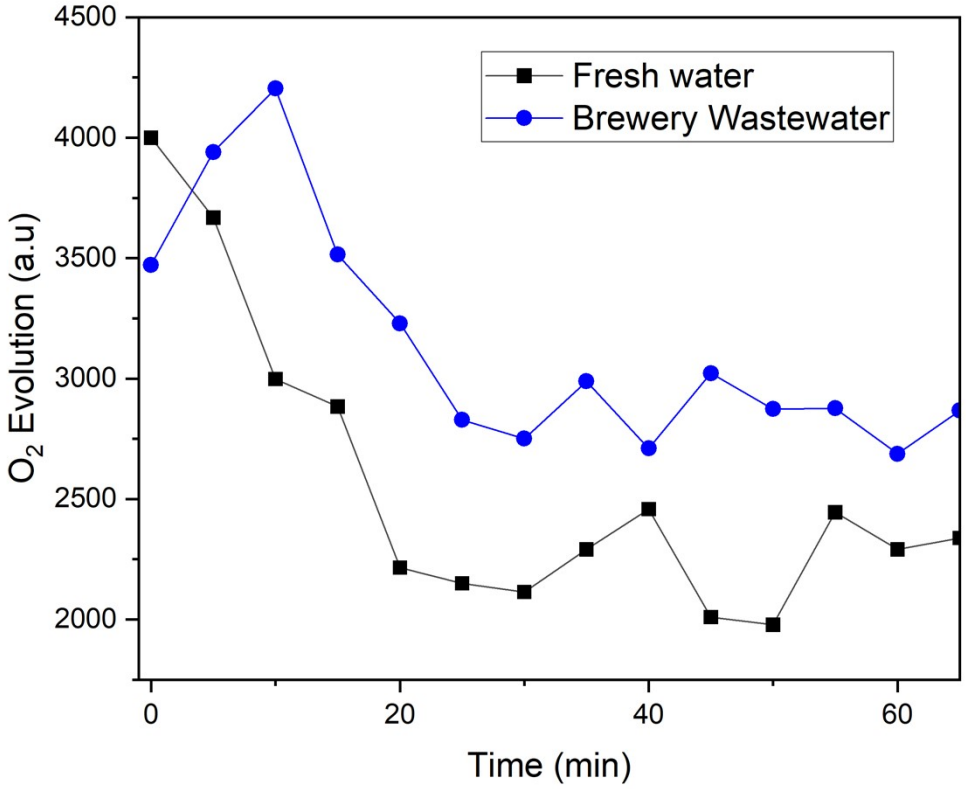

Figure S6. Oxygen evolution of Ni_2Se_3/SS anode measured from electrolysis process using fresh and distillery wastewater based electrolyte. The electrolytes were mixed with 1.0 M NaOH.

S7. Stability test:

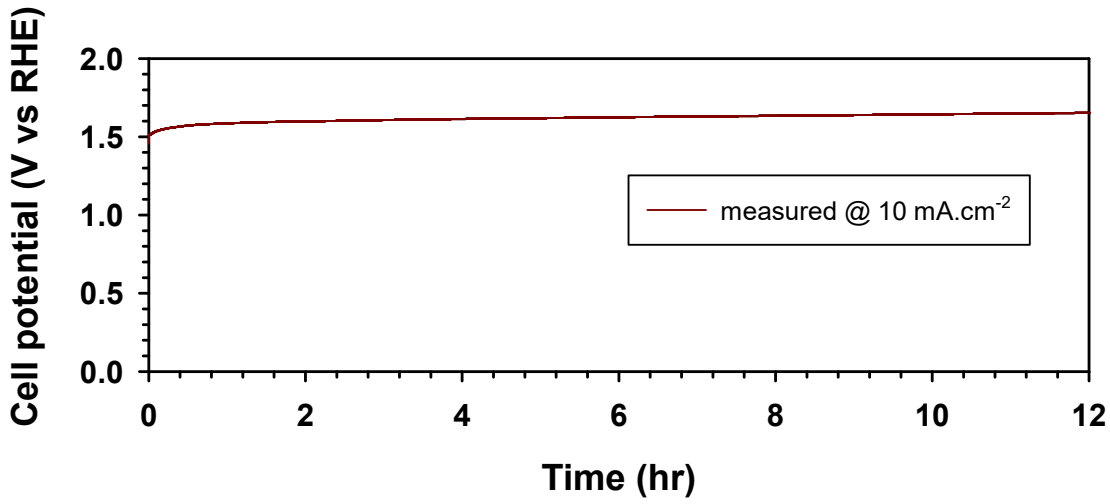

Figure S7. Chronopotentiometry of the Ni_2Se_3/SS anode measured at current densities of 10 mA cm^{-2} in distillery wastewater (1.0 M NaOH).

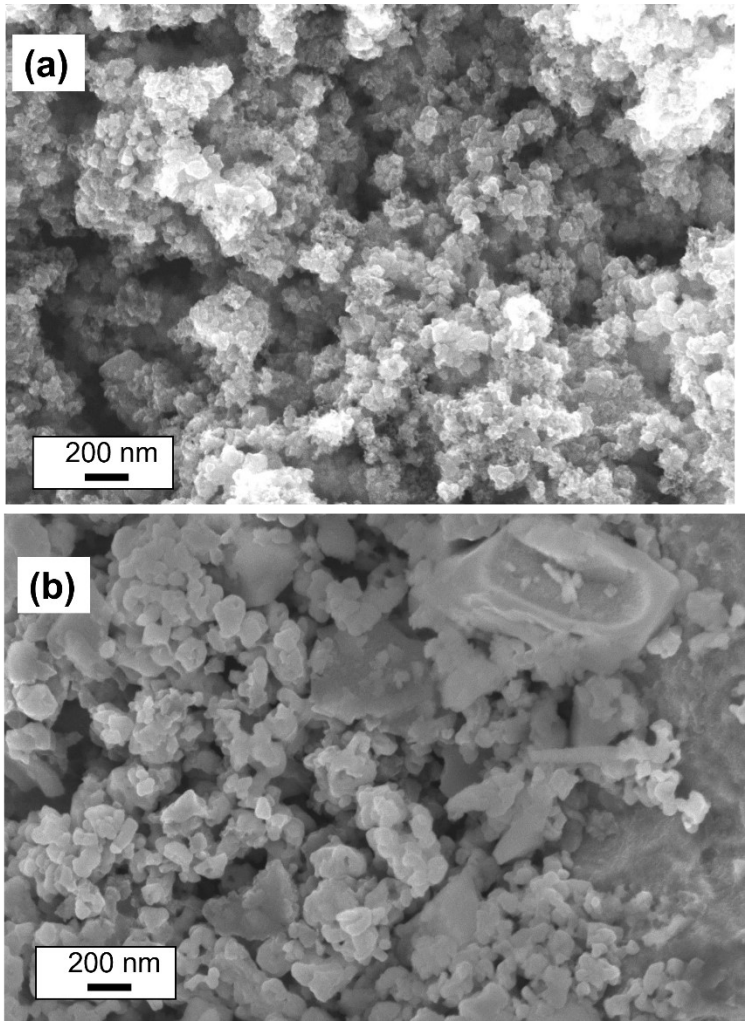

Figure S8. (a) SEM image of Ni_2Se_3 powder (fresh) before and (b) after 12 hr of electrolysis reactions.

S9. Electrochemical parameters estimation:

The electrochemical parameters such as total oxygen turn over (TOF), electrochemical active surface area (ECSA), and actives sites can be estimated based on the previous reports.[1-3]

$$Number\ of\ total\ oxygen\ turnovers = \left(j\frac{mA}{cm^2}\right)\frac{(1C/s)}{1000\ mA}\left(\frac{1\ mol\ e^-}{96845.3C}\right)\left(\frac{1\ mol}{4\ e^-}\right)\left(\frac{6{:}023\ x\ 10^{23}\ molecules\ of\ O_2}{1\ mol\ of\ O_2}\right) \quad (1)$$

$$= \left(10\frac{mA}{cm^2}\right)\frac{(1C/s)}{1000\ mA}\left(\frac{1\ mol\ e^-}{96845.3C}\right)\left(\frac{1\ mol}{4\ e^-}\right)\left(\frac{6{:}023\ x\ 10^{23}\ molecules\ of\ O_2}{1\ mol\ of\ O_2}\right)$$

Number of total oxygen turnovers= $\mathbf{1.56\ x\ 10^{16}}$

Electrochemical surface area (ECSA):

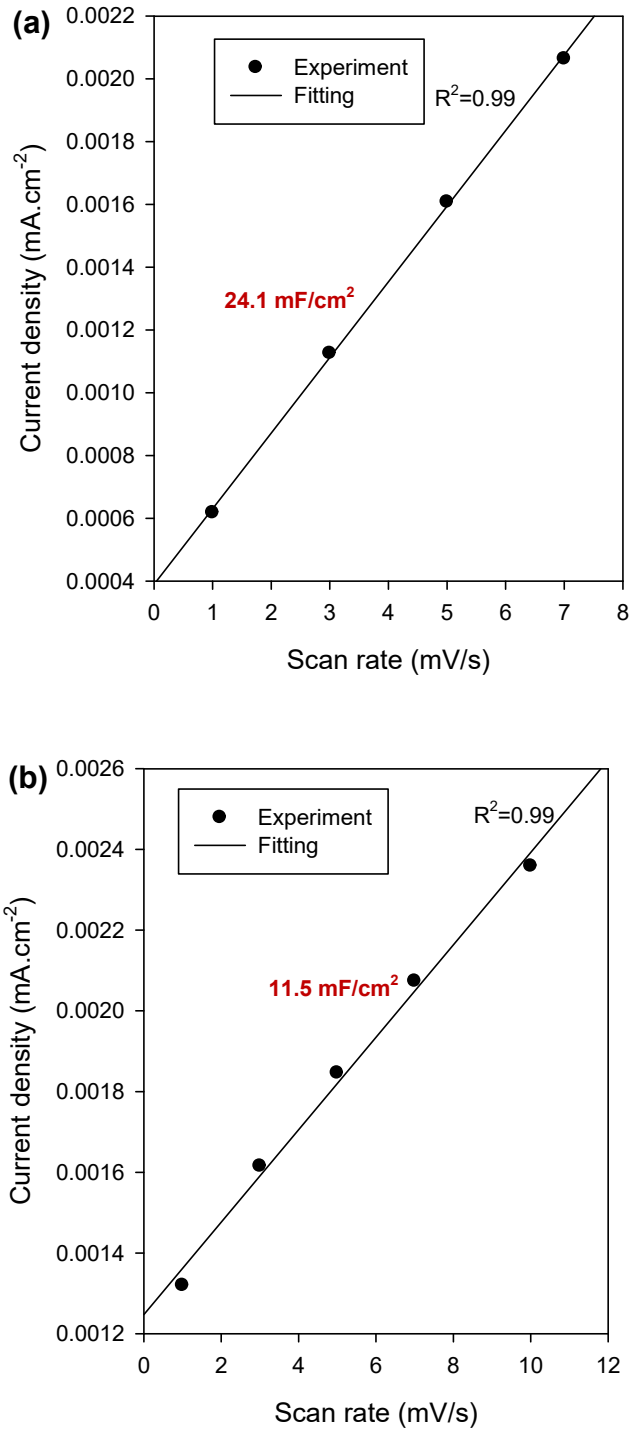

Figure S9. The measured capacitive currents plotted as a function of scan rate (a) distillery wastewater and (b) freshwater.

The electrochemical active surface area (A_{ECSA})

$$A_{ECSA} = (C_{dl})/(C_s) \quad (2)$$

The slope value of the liner fitting from Figure S10 (a) provides the Cdl value in mF/cm^2. The estimated Cdl value is 24.1 mF/cm^2 for freshwater electrolyte. The specific capacitance (Cs) is a constant value dependent on the material and the electrolyte solution (alkaline or acidic).

For this experiment, the C_s value for NiSe was held constant at 0.04 mF.cm^{-2} adopted from the previous report.[4]

A_{ECSA} = 0.1158 (mF.cm^2)/ 0.04 (mF.cm^2) per cm$^2_{ECSA}$ (3)

A_{ECSA} = **2.9 cm$^2_{ECSA}$**

Actives sites per real surface area of NiSe:

$$Active\ sites = \left(\frac{\frac{2\ atoms}{unit\ cells}}{\frac{62.2 Å^3}{unit\ cells}} \right) \quad (4)$$

The volume of the NiSe unit cells is 62.2 Å^3. This value is adopted from the previous report by Unoki et.al.[5]

Active sites = **3.45 x 10^{14} atoms cm$^{-2}_{real}$**

Turnover frequency (TOF)

TOF = (Total oxygen turnovers(cm^{-2})/(active sites density) (5)

TOF = (Total oxygen turnovers(cm^{-2})/(active sites x ECSA) (6)

TOF = (1.56 x 10^{16}) /(3.45 x 10^{14} atoms cm$^{-2}_{real}$ x 2.9 cm$^2_{ECSA}$)

TOF = **4.05** (for over potential @10mA.cm^2)

References:

1. J. Kibsgaard and T. F. Jaramillo, *Angewandte Chemie International Edition*, 2014, **53**, 14433-14437.
2. J. W. D. Ng, M. García-Melchor, M. Bajdich, P. Chakthranont, C. Kirk, A. Vojvodic and T. F. Jaramillo, *Nature Energy*, 2016, **1**, 16053.
3. A. Karmakar and S. Kundu, *Materials Today Energy*, 2023, **33**, 101259.
4. R. Andaveh, A. Sabour Rouhaghdam, J. Ai, M. Maleki, K. Wang, A. Seif, G. Barati Darband and J. Li, *Applied Catalysis B: Environmental*, 2023, **325**, 122355.
5. K. Unoki, A. Yoshiasa, G. Kitahara, T. Nishiayama, M. Tokuda, K. Sugiyama and A. Nakatsuka, *Acta Crystallogr C Struct Chem*, 2021, **77**, 169-175.