Supporting Information

Cathodic disintegration as an easily scalable method for the production of Sn and Pb based catalysts for CO_2 reduction

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SUPPLEMENTARY FIGURES AND TABLES

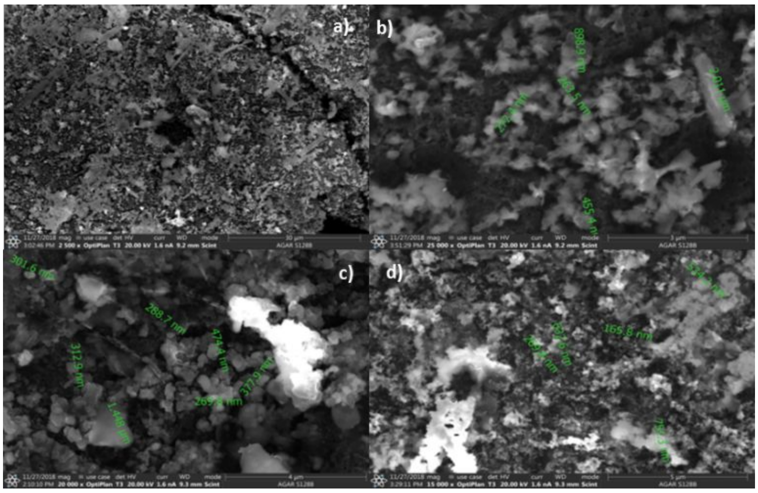

Figure S1. Catalyst morphology and distribution on GDEs a) overview of Pb catalyst: rods and irregular particles are predominant b) zoom-in on Pb catalyst c) Sn catalyst on GDE, consisting mostly of irregularly shaped particles d) Sn50Pb50 catalyst on GDE, similar to Sn only one.

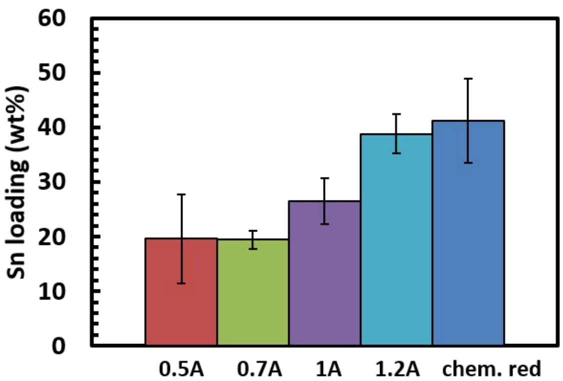

Figure S2. Sn loading on the carbon support estimated from EDX analysis.

Disintegration current	Charge passed	Weight loss
1250 mA/cm²	108C	13.7 mg
1875 mA/cm²	108C	20.47mg
2500 mA/cm²	108C	38.81mg

Table S1. weight loss of Sn wires in 0.1M NaOH at different currents but same charge passed.

Catalyst	Starting V	Starting power	Reaction time
Sn/C 0.5A (1042 mA/cm²)	15.5 V	7.75 W	16 min
Sn/C 0.7A (1458 mA/cm²)	19 V	13.3 W	10.5 min
Sn/C 1A (2083 mA/cm²)	20.5 V	20.5 W	8 min
Sn/C 1.2A (2500 mA/cm²)	20.5 V	24.6 W	6.5 min

Table S2. Summary of reaction conditions for the cathodic disintegration synthesis. The current densities are calculated on the basis of the 0.48 cm² area of wire exposed to the electrolyte. This current density is only valid with the starting geometry of the wire, which is going to change during corrosion. The starting V of Sn/C 1A and Sn/C 1.2A is the same (maximum V reachable by the power supply). This was achieved by reducing the distance between anode and cathode and therefore the ohmic drop between the two.

Calculation of atom efficiency of the synthesis. The atom efficiency is a useful indicator, commonly used in organic synthesis, which describes how many of the atoms present in the reagents can be found in the product. Any atom or molecule remaining in the reaction mixture which is not a desired product is waste and needs to be disposed of. The atom efficiency can be calculated from the stoichiometrically balanced chemical reaction. To calculate the atom efficiency we utilized the following chemical reactions.

CHEMICAL REDUCTION:

$$SnCl_2 + 2\ NaBH_4 + 6\ H_2O \longrightarrow Sn + 2\ NaCl + 2\ B(OH)_3 + 7\ H_2 \qquad (S1)$$

In this case, we assumed that water would take part in the reaction since the ethylene glycol used for the synthesis was not anhydrous and the Sn salt contained water being in dihydrate form.

In the case of the cathodic disintegration we are assuming that the production of metallic particles goes through the formation and immediate oxidation by the aqueous electrolyte (with production of hydrogen) of unstable Zintl phases. We calculated the atom efficiency basing the calculation on two possible cluster anion candidates: the most well documented one (Sn_9^{4-}) and the one that was most unfavorable for our calculation (i.e. with the worst negative charge to number of Sn atoms in the cluster ratio, being Sn_4^{4-}).

CATHODIC DISINTEGRATION:

Cathode half-reaction

$$9(4)\ Sn + 4e^- + 4\ Na^+ \longrightarrow Na_4Sn_{9(4)} + 4\ H_2O \longrightarrow Sn_{9(4)} + 4\ Na^+ + 4\ OH^- + 2\ H_2 \qquad (S2)$$

Anode half-reaction

$$4\ OH^- \longrightarrow O_2 + 4\ e^- + 2\ H_2O \qquad (S3)$$

Overall reaction

$$9(4)\ Sn + 2\ H_2O \longrightarrow Sn_{9(4)} + 2\ H_2 + O_2 \quad (S4)$$

For all the reactions it is left implicit the subsequent agglomeration of the Sn atoms or clusters into larger particles. In the case of the particles produced with disintegration we are also assuming that the clusters are oxidized by the water and coalesce into particles before being captured by the carbon.

Using the formula for the atom efficiency = $$\frac{\Sigma\ MW\ desired\ products}{\Sigma\ MW\ all\ reagents} * 100 \quad (S5)$$

we get a value of 31.8% for the chemical reduction route, 96.7% for the cathodic disintegration considering the Zintl phase based on Sn_9^{4-} and 92.9% considering the Zintl phase based on Sn_4^{4-}.