ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Low-energy formic acid production from CO₂ using electrodeposited tin on GDE

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Date, Author	Electrodes	Electrolytes	j and time	E _{WE} or E _{Cell}	Product (max efficiency)
2016, This study	Sn dep GDE, 10cm ² , 3mg.cm ⁻² , ^{vs.} DSA	0.5M NaHCO ₃ at 25°C /cath 0,5M NaOH /anolyte 10ml.min ⁻¹ CO ₂ ,	7,7 – 10mA.cm ⁻ ² , 4h – 7h	-1,2 to 3V _{cell}	71% HCOOH & 22% CO at -1.05 V _{RHE}
2014, Wang, Qinian	Sn on GDE, 7 cm ² , 5mg.cm ⁻² , 50wt%Nf ^{vs.} Pt sheet 1cm ²	0.5M KHCO ₃ at 25ml.min ⁻¹ /cath&anoly, $30ml.min^{-1}$ CO ₂ ,	18mA.cm ⁻² , 0,5h	-1,4 to - 2,2V _{AgCl}	72,9% HCOOH at -1,8V _{AgCl}
2014, Alvarez	Sn on GDE, 10cm ² , 1,5mg.cm ⁻² , 1:1%Nf vol ^{vs.} DSA	0.45M KHCO ₃ + 0.5M KCl /cath, 1M KOH / anoly, 0,57 ml.min ⁻¹ .cm ⁻²	40mA.cm ⁻² , 1,5h	-3.2 to - 6.1V _{cell} -1,54 to - 2.55V _{AgCl}	70,5% HCOOH at -1,54V _{AgCl}
2014, Wu, Jingjie IV	Sn spray on GDL, 4cm ² , 0,67-6,55mg.cm ⁻ ² , 20wt% Nf ^{vs.} Pt foil	0.5M KHCO ₃ at 25°C /cath&anoly, 45ml.min ⁻¹ CO ₂ ,	< 30mA.cm ⁻² , 0,5h	-1,6V _{SCE}	72% HCOOH at -1,6V _{SCE}
2013, Prakash& Olah	Sn on GDE, 9cm ² , 0.7 mg cm ⁻¹ over the GDL, 1:1% Nf ^{vs.} Pt wire	0.5M NaHCO ₃ at 25°C /cath&anoly, 4ml.min ⁻¹ CO ₂ ,	27mA.cm ⁻² , 0,23h	-1,6V _{NHE}	70% NaHCOO at -1,6V _{SCE}
2013, Wu, Jingjie III	Sn on GDE, 4cm ² , 2mg.cm ⁻² ^{vs.} Pt on GDE, 0,3mg.cm ⁻²	0.1M KHCO ₃ at 7ml.min ⁻¹ /cath&anoly, 45ml.min ⁻¹ CO ₂ ,	2,75mA.cm ⁻² , 2h	-1,2V _{cell} * *H ₂ in anode compartmen t (not H ₂ O)	64% HCOOH 25% CO
2011, Kanan & Chen	Sn dep on Ti foil & Sn foil 2cm2 ^{vs.} Pt gauze, NOT FLOW CELL	0.5M NaHCO _{3 ph 7.2} /cath 0,5M NaOH /anoly SELEMION /Anion exch. memb., 5ml.min ⁻¹ CO ₂ ,	1,8mA.cm ⁻² , 10h	-0,7V _{RHE at ph} ^{7,2} (-1,3V _{AgCI})	25% HCOOH - 0,7V _{RHE ph7.2} 60% CO >85% CO2 reduction
2011, Lee & Machund a	Sn dep GDE, 9cm ² , ^{vs.} Pt plate	n/a /cath H ₂ 10 ml.min ⁻¹ + N ₂ 90 ml.min ⁻¹ /anoly 50ml.min ⁻¹ CO ₂ ,	2mA.cm ⁻² , 1h	-1,6V _{cell} * *H ₂ in anode compartmen t (not H ₂ O)	12% HCOOH at -1.6V (cell)
2007, Li & Oloman	Sn dep on Cu wire mesh, big scale,	0.45M KHCO ₃ /cath,	22mA.cm ⁻² ,	-2.7 to - 4.3V _{cell}	91 to 63% HCOOH
1987, Mahmood	Sn on GDE, 3,2cm ² , ^{vs.} Carbon rod	50g/L Na ₂ SO ₄ pH2, 50-100ml.min ⁻¹ CO ₂	66mA.cm ⁻² , 1,05h	-1,8V _{SCE}	57% HCOOH at 1,8V _{SCE}

Table S1. Summary of the literature on Sn-GDE for CO2R in recent years



Figure S1. FE-SEM images of Sn catalyst electrodeposited at different current densities. Total charge: 4.5 C cm⁻².



Figure S2. XRD pattern of Sn-GDE obtained by electrodeposition on C-Toray ® paper. Reference patterns of β -Sn and graphite were also included.



Figure S3. (a) Overlapping of redox couple potential of tin after correction versus reversible hydrogen electrode potential (b) Current vs potential scans of Sn-GDE electrode inside the EC flow cell showing the stabilization of the native oxide layer in 0.5 M NaHCO3 electrolyte. 1 is the first and 10 is the last scan – conducted at 20 mV s⁻¹ (c) the current vs. potential polarization curves under N2 and CO2 bubbling for Sn-GDE vs nanostructured SnO_x and Sn (5 nm) catalyst results taken from Ref.[1, 2]. The red line is in EC Flow cell operated at 10mL min⁻¹ CO₂ gas flow through Sn-GDE having 10 cm² geometrical electrode areas. The black line is after ohmic drop (iR) correction, R = 1.24 Ohms. Usually ohmic resistances below 1-5 ohms might not be significant in laboratory scale however our system works up to 0.[3]1 A of electrode current. Therefore 1.24 ohms create a big difference after ohmic drop subtraction from the electrode voltage.

[1].S. Zhang, P. Kang and T. J. Meyer, Journal of the American Chemical Society, 2014, 136, 1734-1737.

[2]S. Y. Choi, S. K. Jeong, H. J. Kim, I.-H. Baek and K. T. Park, ACS Sustainable Chemistry & Engineering, 2015, DOI: 10.1021/acssuschemeng.5b01336.



Figure. S4. Conversion efficiency of CO_2 and H_2O into syngas (CO:H2) in 0.5 M NaHCO3 electrolyte solution and 10 mL min⁻¹ CO_2 and electrolyte flow rate.

Once the catalytic stability is reached after 20 minutes, 1:1, 1:1.5 and 1:2 ratio of CO to H_2 gases can be obtained between -0.85, -0,75 and -0.65 V vs. RHE, respectively. At -1.15V vs. RHE, there is still a significant amount of CO gas (7.2 ± 5.5 %) however most of the coulombs passed through the cell spent most likely for HCOO⁻ together with H_2 evolution, indicator of a favoured intermediate path. Another interesting feature can be seen by syngas ratio of the experiment conducted at -0.95 V, which is getting closer to 1:1 until a rapid change arise in the end of first hour shifting 1:2 CO/H₂ ratio.



Figure S5. Cyclic voltammogram (20 mV s⁻¹) on Sn-GDE in the filter-press cell in 0.5 M NaHCO₃ (50 mL min⁻¹) increasing the amount of gas by CO₂ percentage in Ar gas flow (total flow 50 mL min⁻¹). For G/L 2 and 4, 100 and 200 mL min⁻¹ of gas flow was used. in-1) on Sn-GDE electrode



Figure S6 (a) Long term catalytic activity of Sn-GDE conducted under different current densities: 10, 5 and 1 mA.cm⁻² (b) EDX scan and FE-SEM; images of Sn-GDE before and after electroreduction of CO_2 in EC flow cell at -1.1 V_{RHE} in 0.5 M NaHCO₃ electrolyte while both gas and liquid were flowing at 10 mL min⁻¹. There were not any Sulphur traces coming from Nafion additives that usually poison the catalytic sites which is well-known from PEMFC. Also we haven't observed any significant exfoliation of the catalyst from the backbone of the gas diffusion electrode during the simultaneous flow of gas and liquid after the full cell test. The highest catalyst material loss was calculated to be less than 6.2% which is for the test conducted at 50 and 10 mL min⁻¹ gas and liquid flow, respectively.

- [1] S. Zhang, P. Kang, T.J. Meyer, Journal of the American Chemical Society 136 (2014) 1734-1737.
- [2] S.Y. Choi, S.K. Jeong, H.J. Kim, I.-H. Baek, K.T. Park, ACS Sustainable Chemistry & Engineering (2015).

H. Li, C. Oloman, J. Appl. Electrochem. 35 (2005) 955-965.

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