Supplementary Information

Facile deposition of Pt nanoparticles on Sb-doped SnO₂ support with outstanding active surface area for the oxygen reduction reaction

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S1. ECSA comparison for various Pt deposition methods on doped-SnO₂ supports

	Preparation method	Maximum ms- ECSA / m _{Pt} ² g _{Pt} ⁻¹	Ref no.
Catalyst			
$Pt/Sb-SnO_{2-\delta}$ aerogels	Incipient wetness impregnation	45	1
Pt/Nb-SnO _{2-δ}	Colloidal	55	2
Pt/ Nb-SnO _{2-δ}		80	3
$Pt/Ta-SnO_{2-\delta}$		66	4
Pt/ Nb-SnO _{2-δ}		78	5
Pt/Sb-SnO ₂	Chemical reduction	81	6
$Pt/Sb-SnO_{2-\delta}$	Modified polyol	20	7
$Pt/Sb-SnO_{2-\delta}$		5	8
$Pt/Sb-SnO_{2-\delta}$ aerogels		35 ± 5	9
Pt/Nb-SnO _{2-δ} loose tubes	Microwave-assisted polyol	47	10
$Pt/Sb-SnO_{2-\delta}$ loose tubes		44	10
Pt/Nb-SnO ₂	Heat treatment of Pt(acac) ₂	66	11
Pt/Sb-SnO _{2-δ} (polyol)	Polyol	33 ± 6	This work
$Pt/Sb-SnO_{2-\delta}$ reduced	In-house OMCD	101 ± 4	

Table S1 Summary of ECSA values reported for Pt/doped-SnO₂ catalysts obtained from various Pt deposition methods.

S2. Structural characterisation of the ATO nanopowders

Fig. S2.1 shows the powder X-ray diffraction (XRD) patterns of both the as-received and pre-reduced ATO nanopowders used as support materials in this study.



Fig. S2.1 XRD patterns for as-received and pre-reduced ATO support nanopowders. Data for rutile SnO₂ reference line positions shown by black dashed lines.

For both samples, the indexed diffraction lines are associated with a single phase tetragonal rutile-type SnO_2 structure (PDF No. 01-070-6995). As no additional metallic antimony or oxidic phases (e.g. SbO_2 , Sb_2O_3 or Sb_2O_5) were observed, the Sb-dopant atoms are assumed to be incorporated into the SnO_2 lattice. The mean crystallite size calculated using the standard Scherrer equation¹² based on the line broadening of the (110), (101) and (211) lines were 10.7 nm, 12.1 nm and 11.4 nm, respectively, showing the uniform crystallinity and shape of the oxide powder. For the pre-reduced ATO powder, a small additional crystalline secondary phase became evident that was associated with pure rhombohedral Sb metal (PDF No. 00-035-0732). Rietveld refinement showed this phase to consist of large Sb crystallites of approx. 170 nm, containing approx. 24% Sb metal segregated from the primary Sb-SnO₂ phase. No such phases were, however, detected using transition electron microscopy (TEM) analysis. A specific surface area of approx. 66 m² g⁻¹ was found by BET analysis, and an *ex situ* electronic conductivity of 6x10⁻⁴ S cm⁻¹ was obtained for as-received ATO nanopowder.

S3. Structural characterisation of the 20 wt.% Pt/VC catalyst

Fig. S3.1 shows the XRD pattern of the Vulcan XC-72R (VC) carbon supported Pt nanoparticles with 20 wt.% Pt metal loading (20 wt.% Pt/VC). Pt diffraction lines indexed for the face centered cubic (fcc) structure were clearly identified. Estimates for the mean crystallite size were obtained from the Scherrer equation¹² based on the line broadening of the Pt (111) and (220) lines and found to be 3.3 nm and 3.1 nm respectively.



Fig. S3.1 XRD pattern for 20 wt.% Pt/VC electrocatalyst powder.

Fig. S3.2a-c show TEM images of 20 wt.% Pt/VC catalyst at different magnifications. Fig. S3.2d shows the particle size distribution histogram. Pt particles were observed to be roughly spherical and evenly distributed across the surface of the VC carbon support, for which a specific surface area of approx. $225 \text{ m}^2 \text{ g}^{-1}$ was determined using BET analysis. A Pt particle size range between 2 and 6.5 nm was determined with a mean particle size of $3.7 \pm 0.8 \text{ nm}$. Lattice fringes visible in the TEM images (e.g. Fig. S3.2c) with a d-spacing of 2.28 Å, consistent with XRD analysis for Pt (111) planes.⁷



Fig. S3.2 Representative TEM images of the as-prepared 20 wt.% Pt/VC electrocatalyst at different magnifications (a-c) and the particle size distribution histogram (d).

S4. H_{upd} double-layer correction vs. CO-baseline



Fig. S4.1 The H_{upd} region of the CVs of 10 wt.% Pt/ATO in N₂-saturated and in CO-saturated 0.1
M HClO₄. The horizontal dashed lines indicate the capacitive double layer currents used as the standard baseline. The vertical dashed line indicates the lower limit of the H_{upd} region.

S5. Structural characterisation of the 10 wt.% Pt/ATO polyol catalyst



Fig. S5.1 a) Representative TEM image of the as-prepared 10 wt.% Pt/ATO polyol electrocatalyst and b) the particle size distribution histogram.



S6. Structural characterisation of ATO supported catalysts

Fig. S6.1 Pt nanoparticle size distributions determined by TEM analysis of a) 5 wt.% Pt/ATO, b) 10 wt.% Pt/ATO, c) 10 wt.% Pt/ATO reduced and d) 20 wt.% Pt/ATO catalysts.

S7. End-of-test characterisation of the 20 wt.% Pt/VC catalyst



Fig. S7.1 Representative bright field TEM images of 20 wt.% Pt/VC after 1000 degradation cycles in the a) glass cell used in this study and b) flow cell used in our previous work.¹³

S8. X-ray photoelectron spectroscopy (XPS) data fitting for the 20 wt.% Pt/ATO catalyst



Fig. S8.1 XPS fit for the 20 wt.% Pt/ATO catalyst.

Supplementary References

- 1. G. Ozouf, G. Cognard, F. Maillard, M. Chatenet, L. Guétaz, M. Heitzmann, P. A. Jacques and C. Beauger, *Journal of The Electrochemical Society*, 2018, **165**, F3036-F3044.
- 2. F. Takasaki, S. Matsuie, Y. Takabatake, Z. Noda, A. Hayashi, Y. Shiratori, K. Ito and K. Sasaki, *Journal of The Electrochemical Society*, 2011, **158**, B1270-B1275.
- 3. K. Kakinuma, Y. Chino, Y. Senoo, M. Uchida, T. Kamino, H. Uchida, S. Deki and M. Watanabe, *Electrochimica Acta*, 2013, **110**, 316-324.
- 4. Y. Senoo, K. Taniguchi, K. Kakinuma, M. Uchida, H. Uchida, S. Deki and M. Watanabe, *Electrochemistry Communications*, 2015, **51**, 37-40.
- 5. Y. Senoo, K. Kakinuma, M. Uchida, H. Uchida, S. Deki and M. Watanabe, *RSC Advances*, 2014, **4**, 32180-32188.
- 6. N. R. Elezović, B. M. Babić, V. R. Radmilović and N. V. Krstajić, *Journal of The Electrochemical Society*, 2013, **160**, F1151-F1158.
- 7. M. Yin, J. Y. Xu, Q. F. Li, J. O. Jensen, Y. J. Huang, L. N. Cleemann, N. J. Bjerrum and W. Xing, *Appl Catal B-Environ*, 2014, **144**, 112-120.
- 8. G. Cognard, G. Ozouf, C. Beauger, G. Berthomé, D. Riassetto, L. Dubau, R. Chattot, M. Chatenet and F. Maillard, *Applied Catalysis B: Environmental*, 2017, **201**, 381-390.
- 9. G. Cognard, G. Ozouf, C. Beauger, L. Dubau, M. López-Haro, M. Chatenet and F. Maillard, *Electrochimica Acta*, 2017, **245**, 993-1004.
- 10. I. Jimenez-Morales, S. Cavaliere, D. Jones and J. Roziere, *Physical Chemistry Chemical Physics*, 2018, **20**, 8765-8772.
- 11. T. Tsukatsune, Y. Takabatake, Z. Noda, T. Daio, A. Zaitsu, S. M. Lyth, A. Hayashi and K. Sasaki, *Journal of The Electrochemical Society*, 2014, **161**, F1208-F1213.
- 12. A. L. Patterson, *Physical Review*, 1939, **56**, 978-982.
- 13. T. Binninger, R. Mohamed, A. Patru, K. Waltar, E. Gericke, X. Tuaev, E. Fabbri, P. Levecque, A. Hoell and T. J. Schmidt, *Chem Mater*, 2017, **29**, 2831-2843.