

ELECTRONIC SUPPLEMENTARY INFORMATION

Electrosynthesis of 2,3-butanediol and methyl ethyl ketone from acetoin in flow cells†

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1. Mass spectra of 3,4-dimethyl-2,5-hexanedione

Sample Name Ch2CL2 **Position** 2 **Instrument Name** GCMS
User Name **Inj Vol** 1 **InjPosition**
Sample Type **IRM Calibration Status** Not Applicable **Data Filename** 20160302-003 EQ-9.D
ACQ Method test.M **Comment** **Acquired Time** 3/2/2016 4:46:38 PM

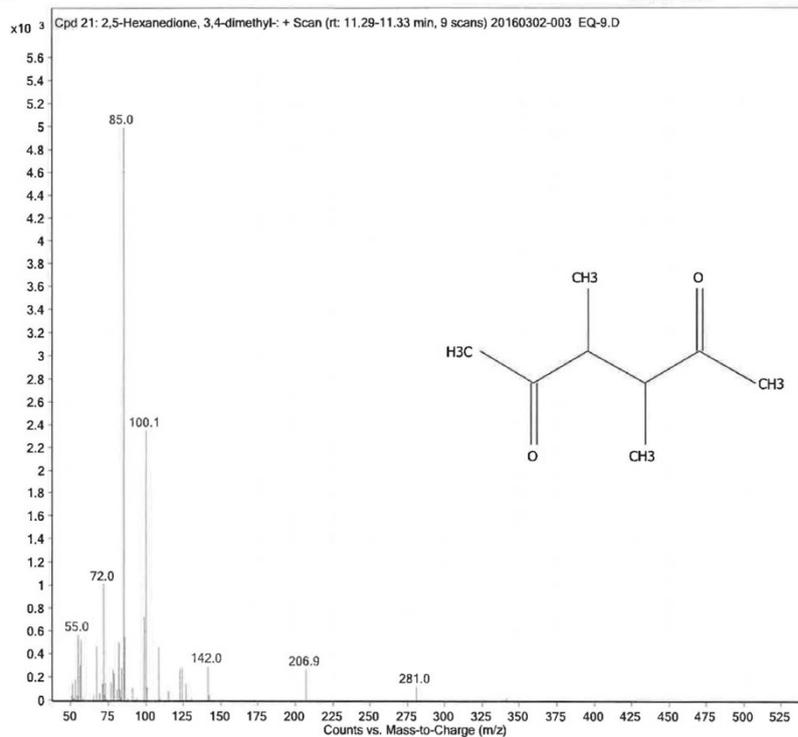


Figure S1. Mass spectra of 3,4-dimethyl-2,5-hexadione as identified by the NIST library

2. EDX results

Table S1. EDX analysis (% atom) of the PtOx before and after H₂ reduction (% atomic).

Sample		C	O	F	Pt	O/Pt
PtOx-Sigracet GDL-24-BC	As deposited	64.59	23.02	4.11	8.28	2.8
PtOx-Sigracet GDL-24-BC	After H ₂ reduction	90.49	0.00	4.87	4.63	-

3. SEM pictures

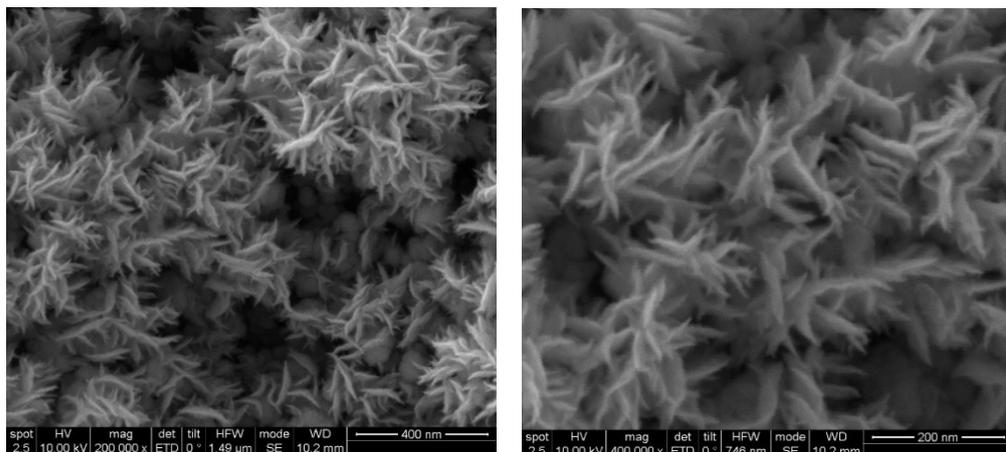


Figure S2. FE-SEM images of the PtOx after the deposition.

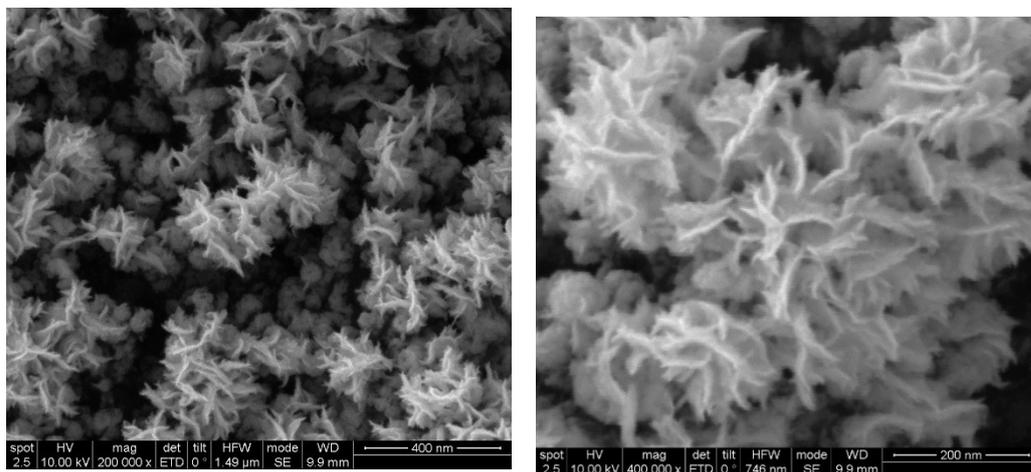


Figure S3. FE-SEM images of the PtOx after hydrogenation.

4. Raman spectra

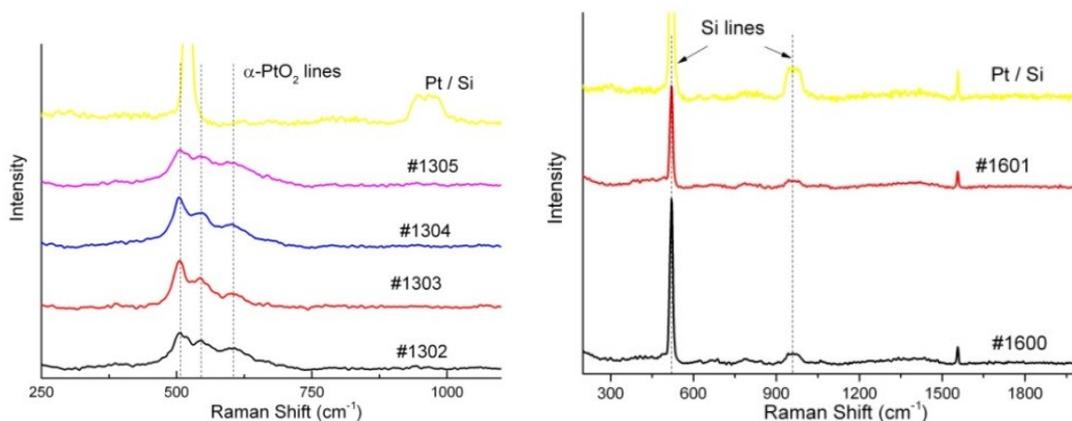


Figure S4. Raman spectra of PtOx (left) and Pt (right) deposited over silicon wafer by physical vapor deposition.

5. Ways for process optimization

For instance, the influence of another electrolytes can be studied for both processes, while more porous GDL-based supports for increasing the surface together with additional combinations of typical hydrogenation catalysts, such as Pt, Ru and Pd, can be used for the electrosynthesis of 2,3-BD. For MEK electrosynthesis, Pb electrochemically deposited on carbon felts or GDL would result in an increase of the electrode surface area that could improve selectivity. Also, taking advantage of the strong difference in acetoin (miscible) and MEK (~270 g. L⁻¹ at 25 °C) water solubilities, the aqueous electrolyte exiting the cell could be send to a solvent extraction step consisting, e.g., in a mixer-settler to remove continuously the MEK synthesized at the cathode by using a good solvent for MEK and poor for acetoin, such as xylenes and toluene. After phase separation the acetoin-containing aqueous phase would be fed back to the cell. Cell design and direct use of the acetoin-containing fermentation broth as a substrate solution are other sources for further improvement. For instance, Momeni, and Nematollahi have designed a parallel-plate filter press flow cell in which the use of a PTFE electrode-electrode spacer with a “snaking” channel pattern allows a long-length channel (1.67 cm per cm² of electrode area, about 4-fold higher than that in our flow cell) providing a high conversion efficiency in a single pass.¹ And

Holzhäuser et al. have reported the successful electrosynthesis of methylsuccinic acid using an itaconic acid-containing fermentation broth as a substrate solution,² thereby reducing energy demand and unit operations relative to the corresponding process using purified itaconic acid from the fermentation broth.

Finally, power consumptions could be dramatically reduced by using a zero-gap cell wherein the aqueous supporting electrolyte is replaced by a solid one consisting in a cation exchange membrane, such as Nafion® 117, placed between both electrodes in contact with them. In this way, the interelectrode gap can be reduced to values as low as 180 µm, reducing dramatically the electrolyte contribution to the total cell voltage. This could be done by using a Polymer Electrolyte Membrane Electrochemical Reactor based on the design of direct organic fuel cells, as shown by Sáez et al. for the electroreduction of acetophenone to 1-phenylethanol.³

6. References

1. S. Momeni and D. Nematollahi, *Green Chem.*, 2018, **20**, 4036-4042.
2. F. J. Holzhäuser, J. Artz, S. Palkovits, D. Kreyenschulte, J. Büchsc and Regina Palkovits, *Green Chem.*, 2017, **19**, 2390-2397.
3. A. Sáez, V. García-García, J. Solla-Gullón, A. Aldaz and V. Montiel, *Electrochem. Commun.*, 2013, **34**, 316-319.