Influence of cathode material on valeric acid electrosynthesis

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The depletion of fossil resources and related climate change due to its usage drives the transition of a fossil-based economy to a bio-based economy and a new world energy economy. Valeric acid (VA) is produced industrially via hydroformylation (oxo-process) of fossil-derived 1-butene and 2-butene followed by oxidation of valeraldehyde and isovaleraldehyde to the corresponding acids (Figure 1).

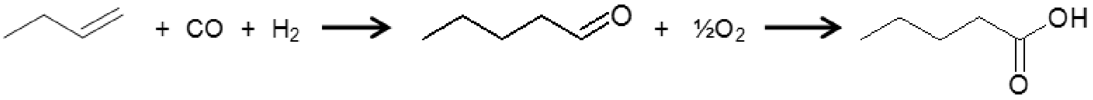

Figure 1: Hydroformylation of 1-butene and subsequent oxidation to valeric acid

Levulinic acid (LA) is one of the renewable platform chemicals and can be derived from lignocellulosic biomass via acid catalysed hydrolysis [1]. The electrochemical reduction of LA to VA (Figure 2) was already discovered in 1911 by Tafel and Emmert [2] at Pb and Hg. This electro-organic reaction was validated at Pb in the 1980's [3] and more recently by other researchers [4]. Advantages of the electro-organic approach are the ambient reaction conditions and one-step approach. Whereas the chemo-catalytic approach involves hydrogenation and dehydration of LA to γ-valerolactone, followed by acid-catalysed ring-opening to 3-pentenoic acid and hydrogenation to VA.

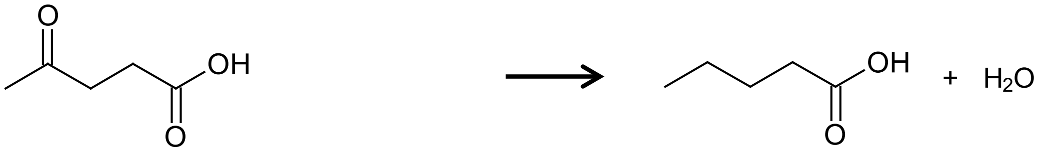

Figure 2: Electrochemical reduction of levulinic acid to valeric acid

The use of active cathodes, such as Pb, forms organometallic compounds, which are subsequently hydrolyzed to the hydrocarbons, similar to the Clemmensen reduction. The selectivity towards the hydrocarbon depends on substrate and electrode material, possible electrode materials include Hg, Pb, Cd, Sn, Zn, Al and Cu. The applicability of other non-precious, but less hazardous metals stimulated us to explore their performance for the electrochemical reduction of LA to VA.

[1] Isikgor & Becer, Polym. Chem., 6 (2015), 4497-4559.
[2] Tafel & Emmert, Zeitschrift für Elektrochemie 17 (1911), 569-572.
[3] Chum *et al.*, J. Electrochem. Soc. 130 (1983), 2508-2510.
[4] Nilges *et al.*, Energy Environ. Sci. 5 (2012), 5231-5235; Xin *et al.*, ChemSusChem 6 (2013), 674-686; Qiu *et al.*, Green Chem. 16 (2014), 1305-1315; Dos Santos *et al.*, RSC Adv. 5 (2015), 26634-26643.