

Hydrogen Generation by Electrochemical Reforming of Alcohols

M. Bellini,^a J. Mahmoudian,^b H.A. Miller,^a M.G. Folliero,^a M.V. Pagliaro,^{a,c} A. Marchionni,^a J. Filippi,^a W. Oberhauser,^a A. Lavacchi,^a F. Vizza.^a

marco.bellini@iccom.cnr.it

^a Istituto di Chimica dei Composti Organometallici - Consiglio Nazionale delle Ricerche (ICCOM-CNR). Via Madonna del piano 10, 50019, Sesto Fiorentino (Firenze), Italy.

^b Department of Industrial Engineering, Università degli Studi di Firenze (DIEF). Via di Santa Marta 3, 50139 Firenze, Italy.

^c Università degli Studi di Siena, Dipartimento di Chimica e Farmacia, Via Aldo Moro 2, 53100 Siena, Italy.



Objectives

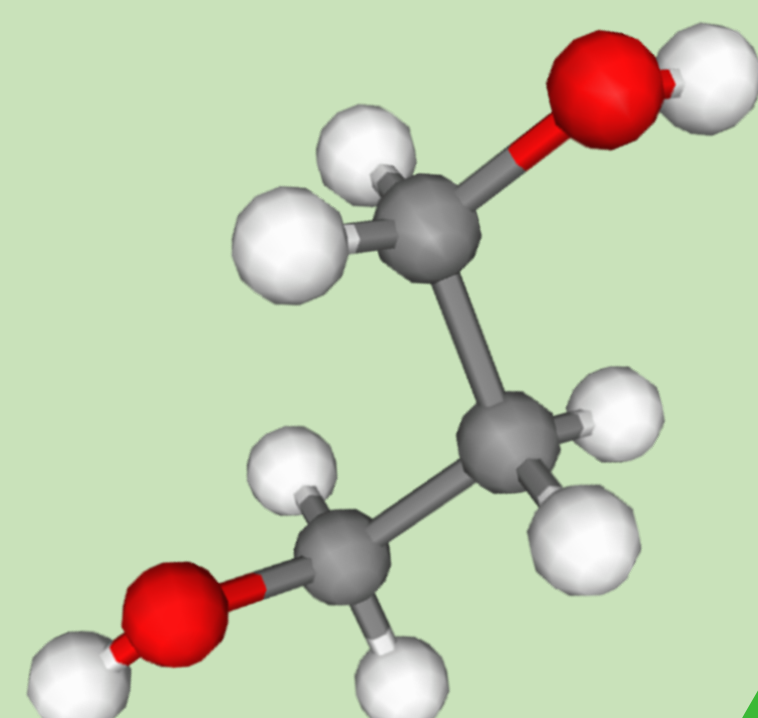
Electrochemical reforming or electroreforming is a technology that combines the production of valuable chemicals from biomass derived starting materials (alcohols) with the production of clean hydrogen at low temperature and atmospheric pressure. [1]

Hydrogen production occurs at energy costs of less than half ($20 \text{ kWh kg}^{-1} \text{H}_2$) when compared to the state of the art water electrolysis ($60 \text{ kWh kg}^{-1} \text{H}_2$) [2]. Of high interest is the formation of partially oxidized intermediates from the alcohols fuel because these compounds are industrial intermediates in cosmetics or polymer industries.

The architecture of the anodic electrocatalyst, the potentials applied to the cell and the operating temperature play a crucial role in driving the selectivity of the alcohol oxidation to chemicals. Here we report a palladium-ceria based anode for the selective conversion of the biomass derived 1,3-propanediol into hydrogen and acrylate. [3]

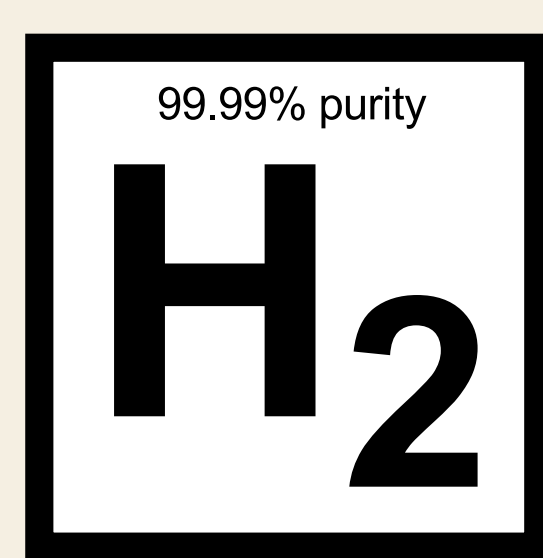


Biomass derived 1,3-propanediol

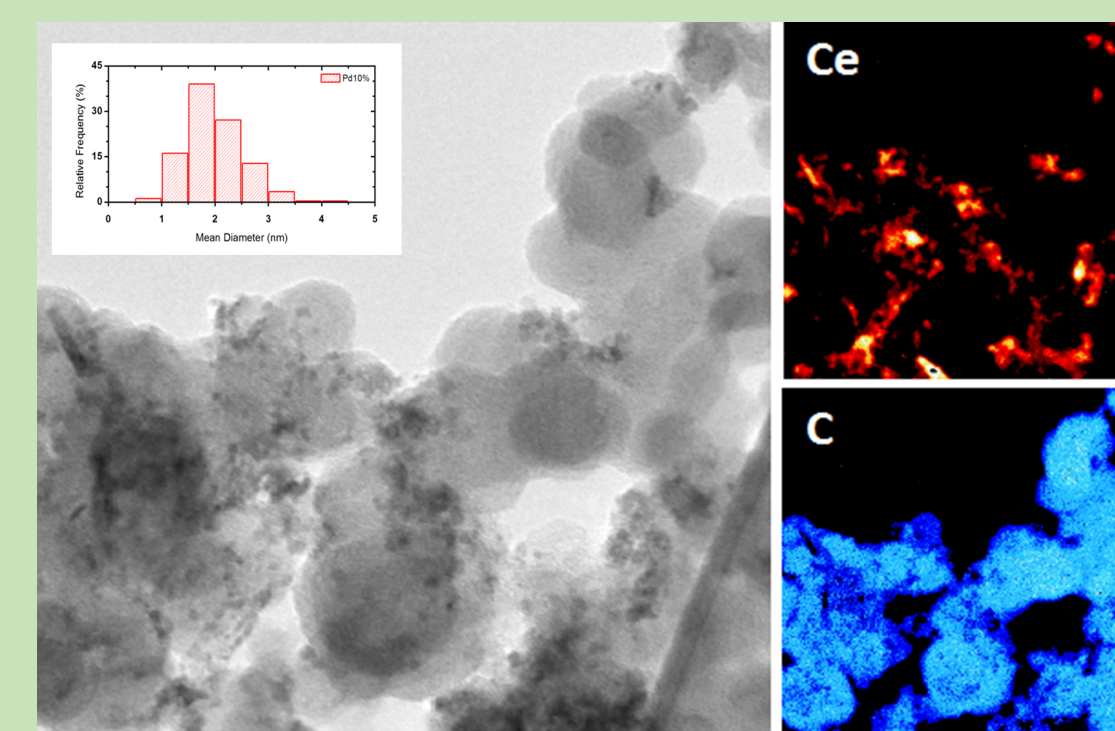
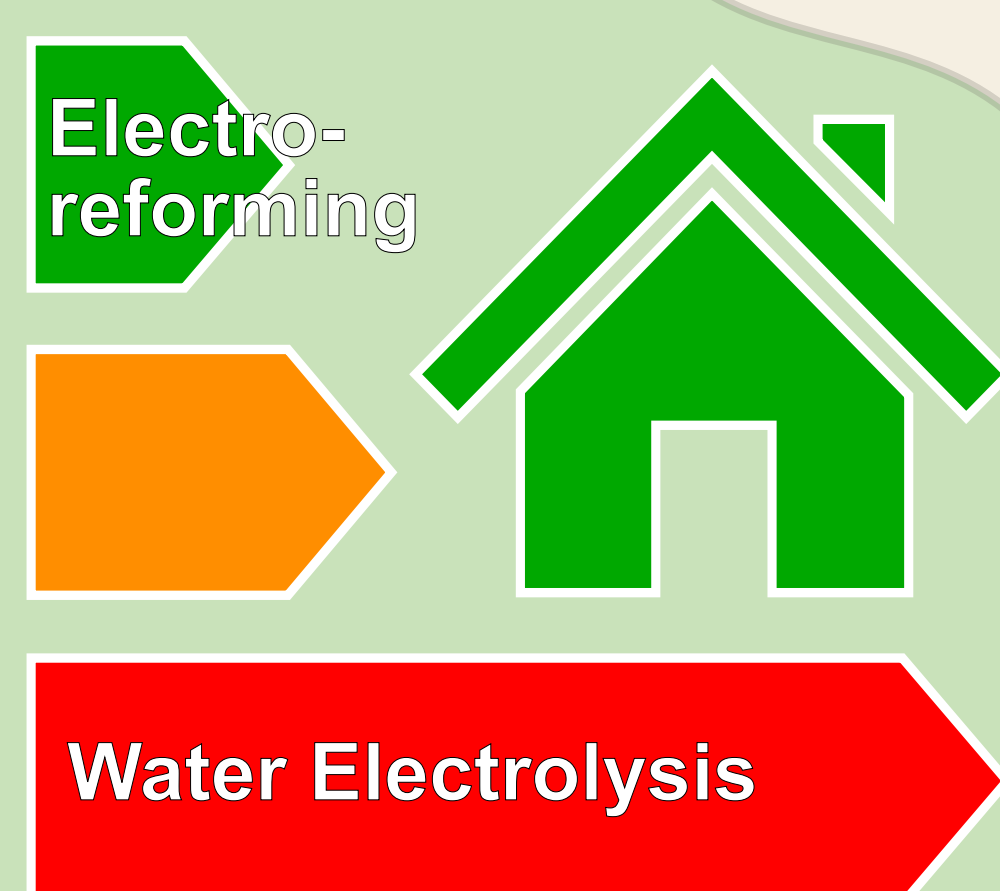


Conclusions

This preliminary study has demonstrated the feasibility of hydrogen and acrylate production using the electroreforming of 1,3-propanediol, an alcohol that currently is produced from biomass derived glycerol and glucose and hence it is a renewable source. In order for the process to be a practical alternative to current petrochemical technologies, the selectivity for the formation of acrylate compared to the other main oxidation products, 3-hydroxy-propanate and malonate, must be optimized and this goal can be achieved by tuning the process conditions.



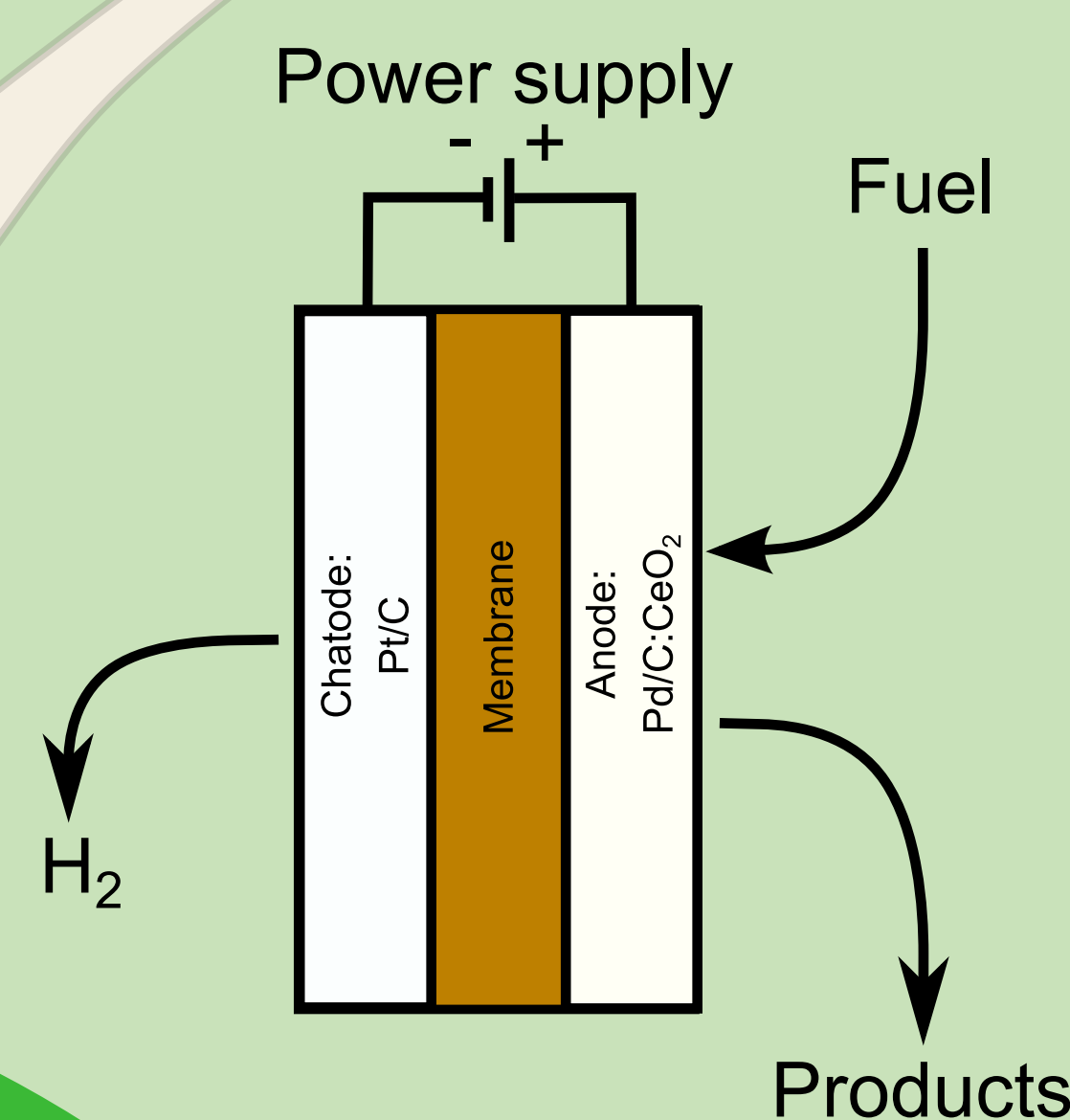
Contemporaneous production of hydrogen and chemicals from the exploitation of biomass derived feedstocks



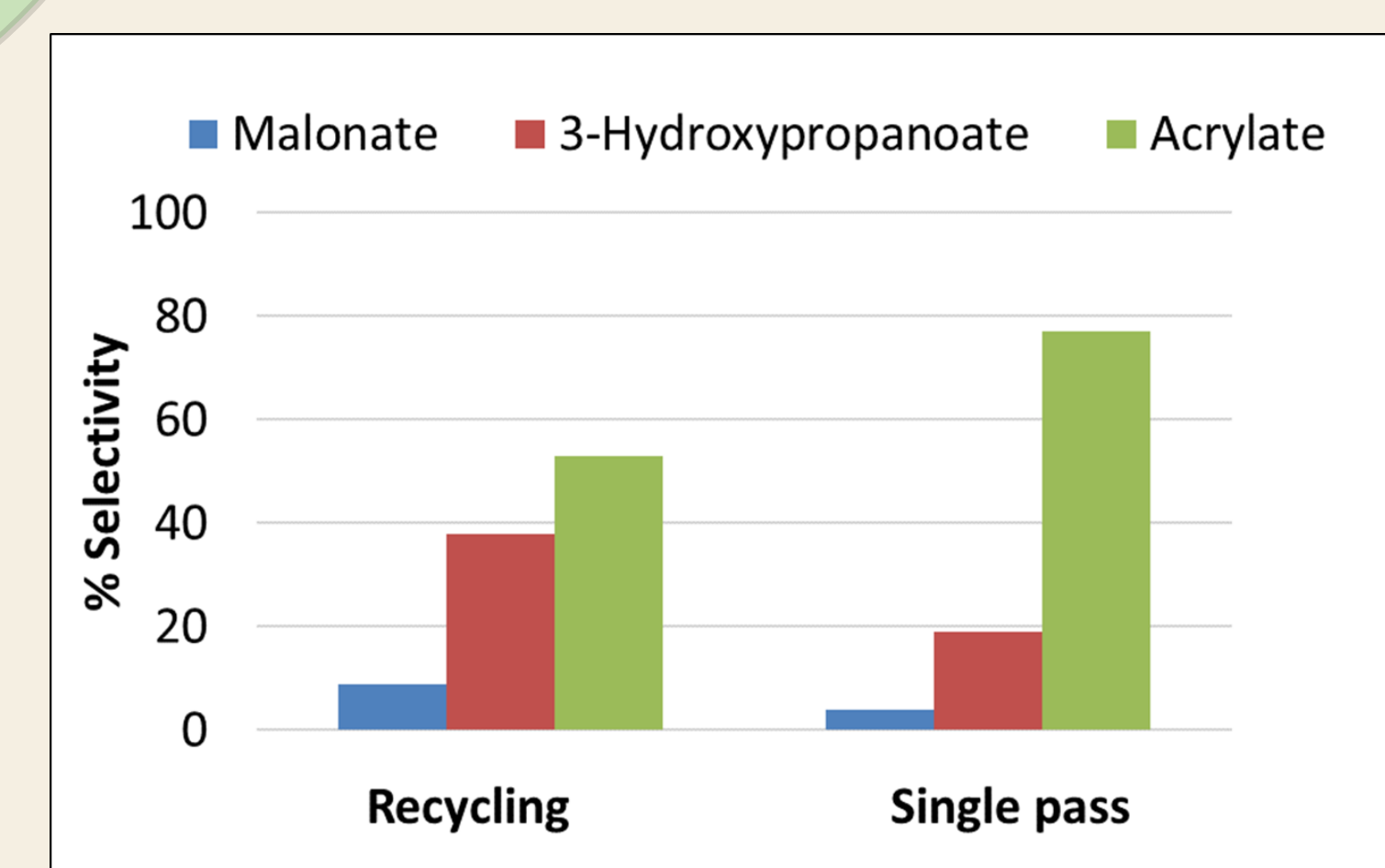
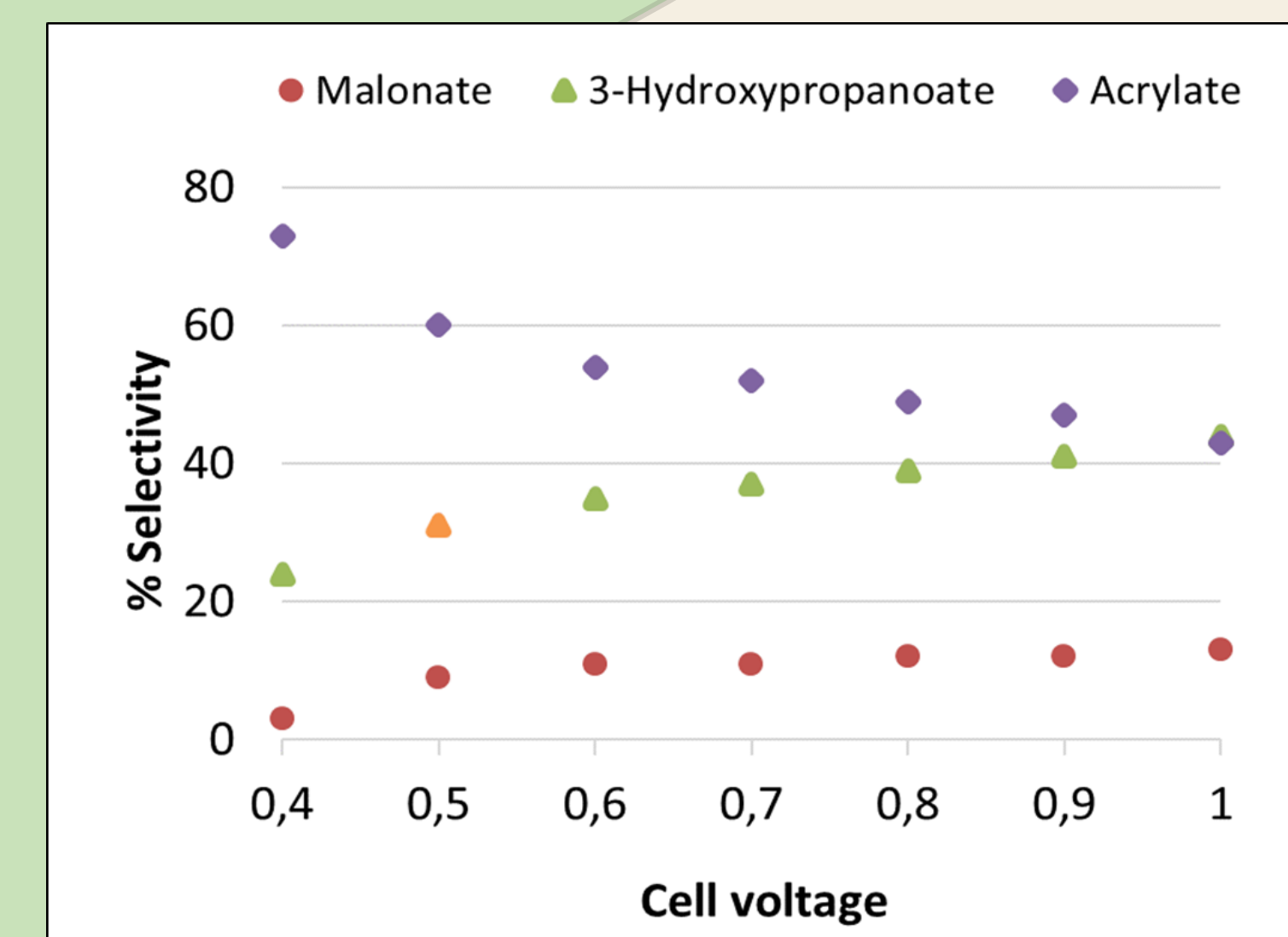
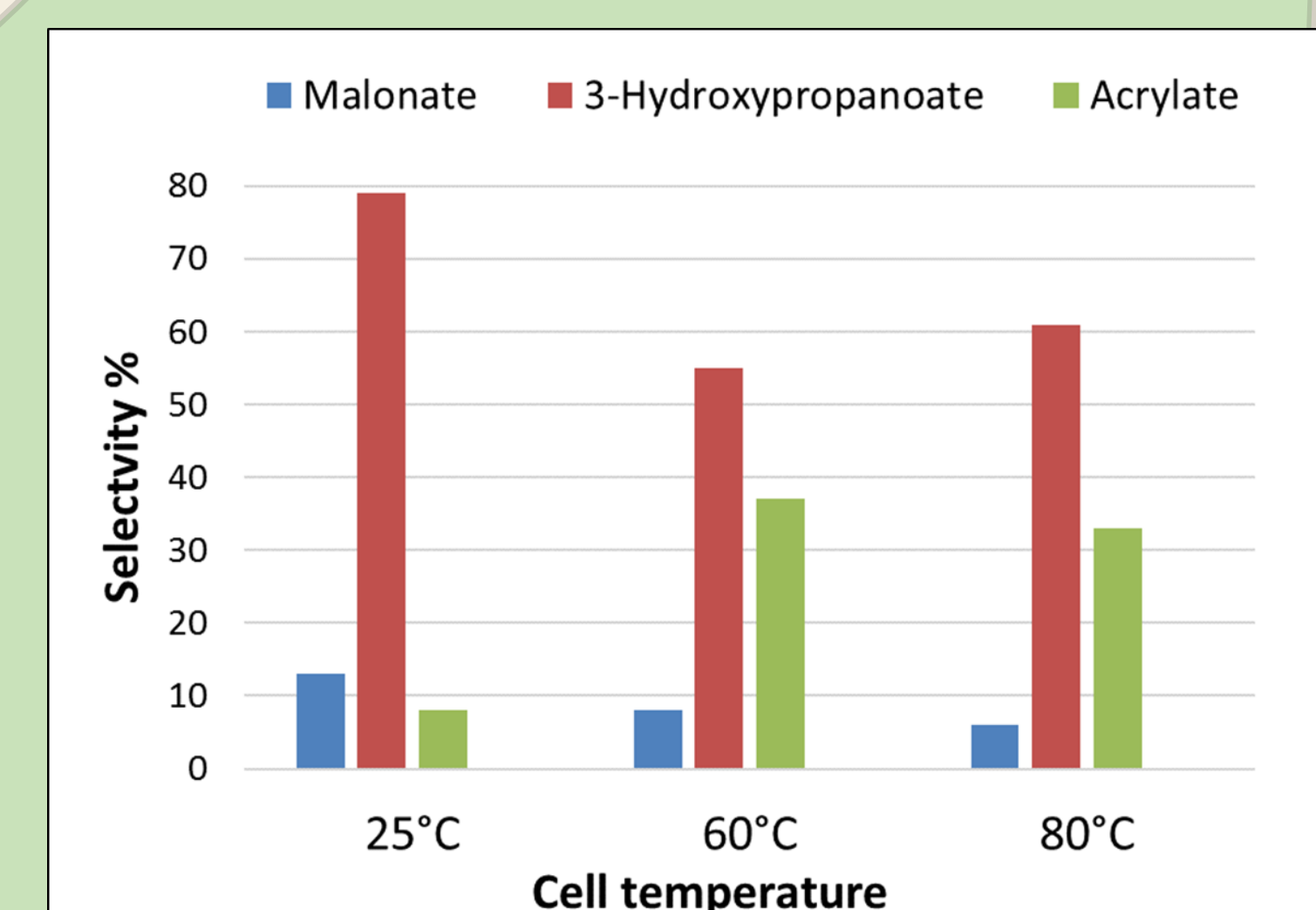
The anode was synthesised following a procedure previously reported in literature [3] and was characterized by TEM images coupled with ESI maps. The anode morphological characterization was complete by XRPD and physisorption analysis.

Methods

A complete electroreformer was set up with a MEA (Membrane Electrode Assembly) composed by a 5 cm^2 Pd (10%)/C:CeO₂ anode (1 mgPd cm^{-2}), a Fumatech anion exchange membrane (Fumasep) and a 5 cm^2 commercial Pt (40%)/C cathode ($0.44 \text{ mgPt cm}^{-2}$). The cell was fed by a presalt pump (1 mL min^{-1} fuel flow) with a 2M 1,3-propanediol 2M KOH aqueous solution.



Results



To drive the selectivity of 1,3-propanediol oxidation to acrylate, several process parameters were modified. Cell temperature, cell potential and flow regime have an influence on the process selectivity: the highest selectivity for potassium acrylate was obtained at 80°C and 400 mV in single pass mode.

References:

[1] A. de la Osa et al. *App. Catal. B - Environ.* **2015**, 179, 276-284.

[2] Y.X. Chen et al. *Nat. Comm.* **2014**, 5, 4036-4041.

[3] J. Mahmoudian et al. *ACS Sustainable Chemistry and Engineering* **2017**, 5, 6090-6098.