N°594 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Fructose upgrading via electrocatalytic hydrogenation to sorbitol

AUTHORS

Jordi CREUS / UNIVERSITY OF GRONINGEN, CHEMICAL ENGINEERING GROUP, ENGINEERING AND TECHNOLOGY INSTITUTE GRONINGEN (ENTEG), UNIVERSITY OF GRONINGEN, NIJENBORGH 4, GRONINGEN
Matteo MIOLA / UNIVERSITY OF GRONINGEN, CHEMICAL ENGINEERING GROUP, ENGINEERING AND TECHNOLOGY INSTITUTE GRONINGEN (ENTEG), UNIVERSITY OF GRONINGEN, NIJENBORGH 4, GRONINGEN
Corresponding author : Paolo P. PESCARMONA / p.p.pescarmona@rug.nl

PURPOSE OF THE ABSTRACT

The use of organic electrosynthesis for biomass upgrading (such as saccharides or sugar alcohols) is gathering increasing attention.1 While the electrochemical oxidation of saccharides (especially glucose) has already gathered substantial attention among the scientific community,2 the reduction of these species seems more complex and only a dozen of studies have reached scientific publication.3 The hydrogen evolution reaction (HER) competes with the hydrogenation of saccharides in the reaction conditions, utilizing a fraction of the electric current and thus limiting the current efficiency the organic conversion.1 The production of sorbitol from glucose was formerly performed via electrolcatalysis involving highly-toxic mercury or lead cathodes to diminish the competition with the HER.4 At the same time, several homogenous-phase, competitive chemical reactions take place such as glucose isomerization and degradation.5 The faster mutarotation and consequent higher concentration of the acyclic form of fructose in contrast to glucose, make the former a more redox-reactive substrate than glucose, appearing as a better candidate for the obtaining of sorbitol via electrochemical methods.

In this communication, a study of the fructose reduction reaction (FRR) is presented, involving the use of Cu as an earth-abundant metal as catalyst in mild alkaline conditions (pH = 11.3). A thorough investigation of the reaction parameters allowed improving control over the reaction pace, thus decreasing the formation of side products from the isomerization and degradation reactions, as well as to decrease the competition with the HER and thus increase the Faradaic efficiency towards sorbitol and mannitol. The use of linear sweep voltammetry (LSV) and chronopotentiometry (CP), coupled with product analysis by high-pressure liquid chromatography (HPLC), allowed evaluating the different reactions taking place. Through a systematic assessment and optimization of the reaction parameters, high current efficiencies of >40% were reached and maintained for 10h electrolysis at i = -20 mA electric current. A control over the formation of chemical conversion species (<2% conversion to glucose and mannose in 10h) has also been achieved by using a buffer electrolyte and a titration pump which allow to keep the pH constant at 11.3±0.3. A two-step potential strategy is followed in order to re-activate the catalyst surface, that allowing achieving an electrochemical conversion >75% in 10h electrolysis. This is the first time that the electrocatalytic FRR is published by using a non-noble metal-based cathode.

FIGURES

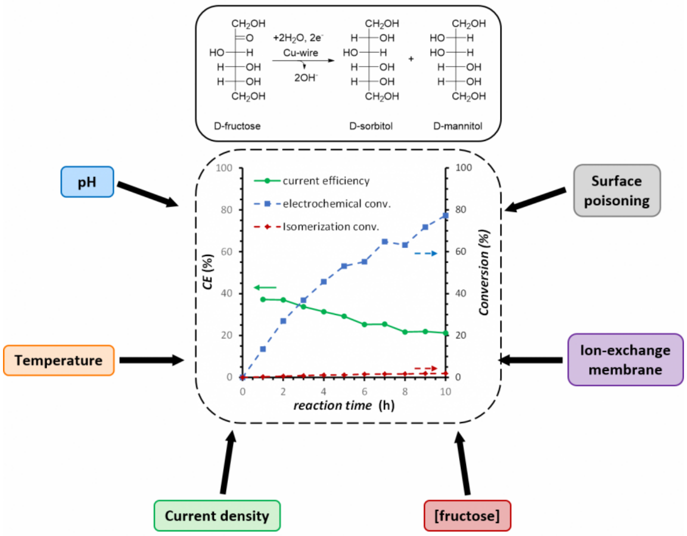

FIGURE 1

Figure 1

Graphical representation containing on top, the electrocatalytic FRR, a plot with the main current efficiency and conversion results, and the studied parameters for the reaction optimization.

FIGURE 2

KEYWORDS

electrocatalysis | biomass upgrading | sorbitol | earth-abundant

---

BIBLIOGRAPHY

(1) Holade, Y.; Servat, K.; Tingry, S.; Napporn, T. W.; Remita, H.; Cornu, D.; Kokoh, K. B. Advances in Electrocatalysis for Energy Conversion and Synthesis of Organic Molecules. ChemPhysChem 2017, 18 (19), 2573–2605.
(2) Gallezot, P. Conversion of Biomass to Selected Chemical Products. Chem. Soc. Rev. 2012, 41 (4), 1538–1558.
(3) Kwon, Y.; Koper, M. T. M. Electrocatalytic Hydrogenation and Deoxygenation of Glucose on Solid Metal Electrodes. ChemSusChem 2013, 6 (3), 455–462.
(4) Kuhn, A. T. Industrial Electrochemical Processes. A Comprehensive Review of Past and Present Industrially Scaled Processes. Herausgeg. von A. T. Kuhn. Elsevier Publishing Comp., Amsterdam-London-New York 1971, 1. Aufl., XXIV, 632 S., Zahlr. Abb. u. Tab., Geb. Dfl. 16. Chemie Ing. Tech. 1972, 44 (18), 1091–1092.
(5) Carraher, J. M.; Fleitman, C. N.; Tessonnier, J.-P. Kinetic and Mechanistic Study of Glucose Isomerization Using Homogeneous Organic Brønsted Base Catalysts in Water. ACS Catal. 2015, 5 (6), 3162–3173.