A Polymer Electrolyte Alcohol Electrosynthesis Cell (PEAEC) Continuously Producing Alcohols from Carboxylic Acids

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Development of electrolyzers converting electricity into chemical energy is one of the current topics in energy-related chemistry. We have focused on alcohol electrosynthesis using ubiquitous carboxylic acids, which are some of the main components of biomass-derived materials, to storage renewable electricity. We previously reported that oxalic acid (OX), a divalent carboxylic acid, is efficiently glycolic converted into acid (GC), а monovalent alcohol, on anatase TiO₂ through four-electron reduction in a two-compartment electrolyzer.¹ However, we believe that the two-compartment electrolyzer that requires an electrolyte, e.g. Na₂SO₄, is not an ideal system to obtain pure alcoholic compounds without separation procedure. One idea to solve this problem is to employ a polymer electrolyte electrolyzer, having a membrane-electrode assembly (MEA), for the alcohol synthesis. To date, however, there is no report on the alcohol electrosynthesis from the carboxylic acids using the polymer electrolyte electrolyzer.

In this study, we report on a fabrication of a polymer electrolyte electrolyzer for the alcohol electrosynthesis, named as "polymer electrolyte alcohol synthesis cell (PEAEC)" by applying a novel cathode, metal mesh tightly connected with porous anatase TiO₂ catalyst, which has both catalytic activity for carboxylic acid reduction and substrate diffusivity. We prepared Ti mesh electrode decorated by the porous anatase TiO₂ catalyst (TiO₂/Ti-M) by employing two-step hydrothermal reactions² with 1 M NaOHaq and water. Figure 1 shows SEM images of the Ti mesh before and after the hydrothermal reactions. After the reactions, fibrous porous TiO₂ (or H₂Ti₂O₅·H₂O after the first step) was formed around the Ti line of the

Ti mesh. TEM observation for the TiO_2 (Figure 1d) revealed that small single crystals of anatase TiO_2 aggregated to form the fibers.

The PEAEC was constructed using the TiO_2/Ti -M as a cathode, Nafion as a polymer electrolyte, and IrO_2 -loaded carbon as an anode (for water oxidation) (Figure 2). We performed electrolysis at constant bias (1.8-3.0 V) under a continuous flow of reaction solutions (OXaq and water on cathode and anode side, respectively). The products are characterized and quantified by HPLC. 100% conversion of the OX was observed by applying 2.4 V bias between both electrodes.

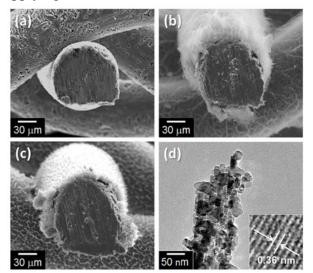


Fig. 1 SEM images of (a) Ti mesh, (b) Ti mesh after the first-step reaction taking 12 h, and (c) after the second-step reaction taking 24 h (TiO₂/Ti-M). (d) A TEM image of a TiO₂ fiber deposited on the TiO₂/Ti-M.

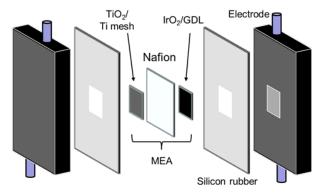


Fig. 2 A schematic illustration of PEAEC.

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