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SELF-SUSTAINABLE PRODUCTION OF HYDROGEN AND CHEMICALS FROM RENEWABLE ALCOHOLS BY ALKALINE ELECTROLYSIS

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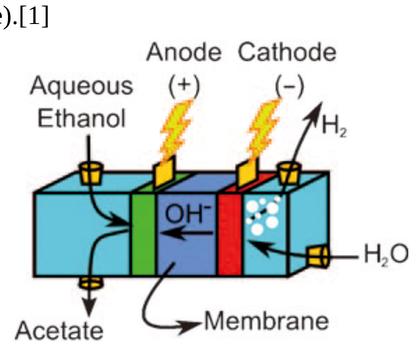
Introduction

The production of hydrogen from renewable alcohols, such as ethanol, glycerol, and ethylene glycol, can be accomplished using alkaline electrolyzers. In these devices the oxidation of the alcohol at the anode (1) is coupled to the production of hydrogen from water at the cathode (2). Furthermore, the anode electrocatalyst can be appropriately designed to promote the partial and selective oxidation of the alcohol to yield valued chemicals. For example for every kg of hydrogen produced from aqueous ethanol the electrolysis cell yields also 25 Kg of potassium acetate, (with a KOH electrolyte).[1]



$$(1)\ CH_3CH_2OH + 5OH^- \rightarrow CH_3COO^- + 4H_2O + 4e^-$$
$$(2)\ 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$
$$(3)\ CH_3CH_2OH + OH^- \rightarrow CH_3COO^- + 2H_2$$

Fig. 1: Simplified illustration of an electrolyzer with an anion-exchange membrane, in which ethanol is converted into acetate at the anode and hydrogen is produced at the cathode.

The alcohol electrolyzer costs about one-third of the amount of energy required by a traditional H_2/O_2 electrolyzer, by virtue of the fact that the production of hydrogen occurs at very low operating voltages (see Fig. 3 for ethanol). By contrast the energy requirement to produce hydrogen from water electrolysis is governed to a large part by the thermodynamic potential (*i.e.* operating voltages are typically over 1.5 V for water electrolysis).

Results and discussion

We have recently reported a new method for enhancing the catalytic activity of supported palladium heterogeneous catalysts.[2] This work demonstrated a novel electrochemical treatment of Pd nanoparticles supported on TiO_2 nanotube arrays (TNTA), that enhances the ethanol electro-oxidation mass specific activity by a factor of ten. The enhancement was attributed to both a decrease in average Pd particle size (Fig. 2) and to an increase in the presence of low coordinated surface Pd atoms.

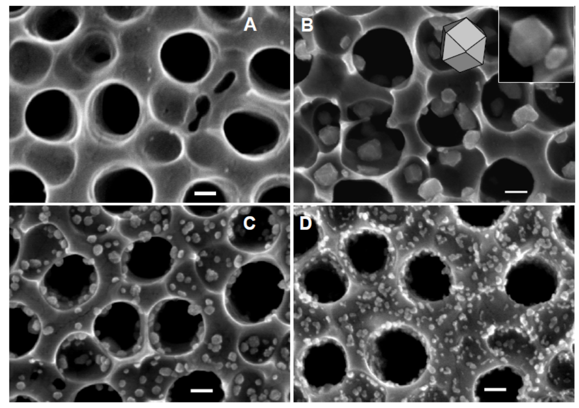


Fig. 2: SEM micrographs of: (A) TNTA substrate, (B) the Pd doped TNTA, (C) and (D) Pd/TNTA after sequential electrochemical treatments (scale bar 50 nm).

Here we describe the application of this material to the anode of an electrolyzer equipped with an anion exchange membrane and a commercial Pt/C cathode (Fig 1).
We will discuss the performance of the electrolyzer fed with a range of renewable alcohols including ethanol (Fig. 3), glycerol and ethylene glycol and also a study of the selectivity towards the production of valuable chemicals from these feedstocks.

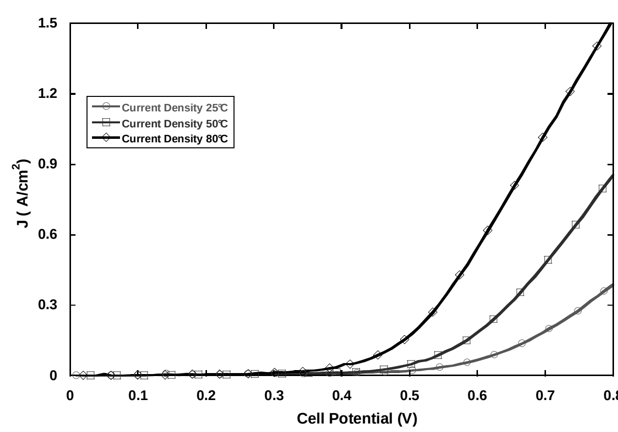


Fig. 3 Variation of current density as a function of applied potential for the alcohol electrolyzer. Electrolyte 2M Ethanol, 2M KOH.

[1] V. Bambagioni, M. Bevilacqua, C. Bianchini, J. Filippi, A. Lavacchi, F. Vizza, P.K. Shen, ChemSusChem 3 (2010) 851.
[2] Y. Chen, A. Lavacchi, S. Chen, F. Di Benedetto, M. Bevilacqua, C. Bianchini, P. Fornasiero, M. Innocenti, M. Marelli, W. Oberhauser, S. Sun, F. Vizza, Angewandte Chemie, 124 (2012) 8628.