Highly Efficient and Highly Selective Electroreduction of Oxalic Acid on Porous TiO_2 for CO_2-Free Energy Cycle

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1. Introduction

An energy cycle composed of chemical energy storage of intermittent renewable energy supply systems such as solar photovoltaic, wind turbine and wave etc. and efficient conversion of electrical energy by fuel cell without emission of CO_2 is essential for achievement of a sustainable carbon-neutral society. Hydrogen offers tremendous potential as a renewable energy carrier. Hydrogen fuel cells provide the essential link between renewable energy sources and sustainable energy services. Hydrogen based economy, however, is fraught with many technical challenges to hydrogen storage, transmission and distribution. Therefore, development of easy handling energy carrier has been required. Recently, a new concept of energy cycle using alcohols as energy carriers has been proposed[1]. However, electric power storage by electrochemical reduction from carboxylic acids to alcohols has never been realized. Here we show highly efficient $4e^-$ electroreduction from oxalic acid (OX, HOOC-COOH) to glycolic acid (GC, HOOC-CH_2OH) using porous TiO_2 spheres (PTSs) for realization of GC based energy cycle.

2. Experimental

PTS was synthesized by calcination of layered protonated titanate (LPT) according to previously reported method[2] with slight modifications. The product was characterized by XRD, TEM, nitrogen adsorption-desorption analysis, STEM-EELS, UV-vis and XPS. Electrolysis of OX was performed by chronoamperometry using a electrode (10 mg catalyst deposited on Ti foil) in 0.03 M OX with 0.2 M Na_2SO_4 at 0.7 V vs. RHE.

3. Results and discussion

STEM image of LPT calcined at 500 °C, denoted by PTS-500, exhibited a spherical aggregate composed of nanorods (Fig. 1a). EELS mapping taken from the area marked by a red square in the STEM image showed that PTS-500 was constituted of purely anatase-type TiO_2 (Fig. 1b). Electrolysis performance by PTSs-500/Ti foil was investigated. It was noted that GC selectivity and Faraday efficiency were 99% and 90%, respectively.

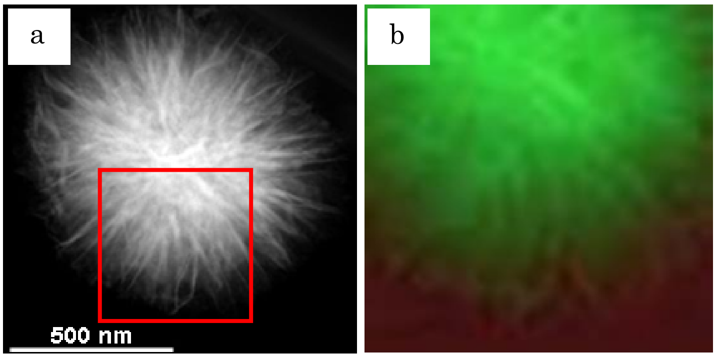

Fig.1 a, STEM and b, EELS mapping of PTS-500. Green portion indicates anatase-type TiO_2.

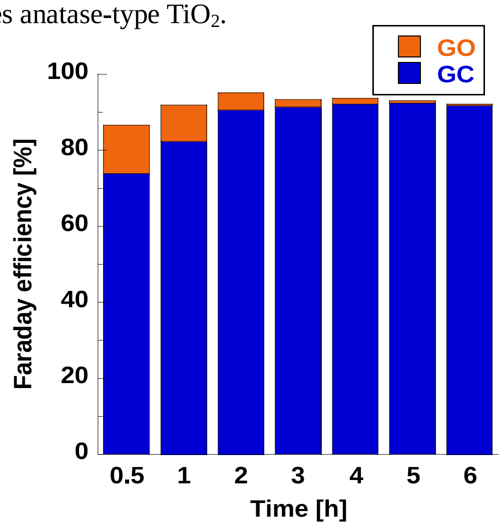

Fig.2 OX reduction using PTS-500.

4. Conclusions

Highly selective and efficient electroreduction from OX to GC was attained using PTS-500 composed of the purely anatase-type TiO_2 at -0.7 V at 50 °C.

References

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2. H. B. Wu, X. W. D. Lou, H. H. Hng, Chemistry A European Journal 18 (2012) 2094.