Oxide catalysts for electronic reduction of oxalic acid toward efficient power storage

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Establishment of an efficient electric power distribution method is the key to realize a sustainable society driven by renewable-energy-based electricity. Recently, electric power storage in high-energy chemicals, called "energy carriers", has received much attention for the efficient storage and on-demand supply of renewable electricity. Here, we demonstrate direct power charge using an alcohol/carboxylic acid redox couple as illustrated in Fig. 1[1, 2]. In this study, glycolic acid (GC), a monovalent alcoholic compound and oxalic acid (OX), a divalent carboxylic acid, are focused due to their stability and transportability as energy carriers. Nanometer-sized TiO_2 with a high specific surface area, which is denoted as porous TiO_2 sphere (PTS), was prepared by calcination of layered protonated titanate at various temperatures based on a report.[3] We conducted electroreduction of OX using PTSs. Both total yields and yields for GC production increased with the calcination temperature up to 500 °C but drastically decreased above 550 °C. STEM-EELs mapping for PTSs revealed that whole grain of an active catalyst is composed only of an anatase phase while a rutile phase forms on the surface of an inactive one, which suggests that detailed structural control is significantly predominant in this process. Then, we optimize reaction conditions and achieved high Faradaic efficiencies for the production of GC from OX on ubiquitous TiO_2 catalysts with high efficiency and selectivity (70-95% Faraday efficiency and >98% selectivity) under mild conditions in the potential region of -0.5 to -0.7 V vs. the RHE at 50 ºC [4, 5]. The most desirable characteristic of this electroreduction is the suppression of hydrogen evolution even in acidic aqueous media (Faraday efficiency of 70–95%, pH 2.1). The detailed observation of TiO_2 catalysts using scanning TEM and eels techniques provided a mechanistic insight into this highly selective catalysis.

Recently, we succeeded in the production of GC via the electrochemical reduction of OX and electrooxidation of water with the help of renewable light energy for the first time.[6]

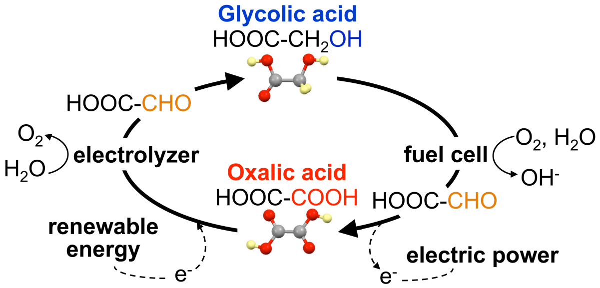

Fig. 1 Carbon-neutral power charge and discharge using the **GC**/**OX** redox couple.

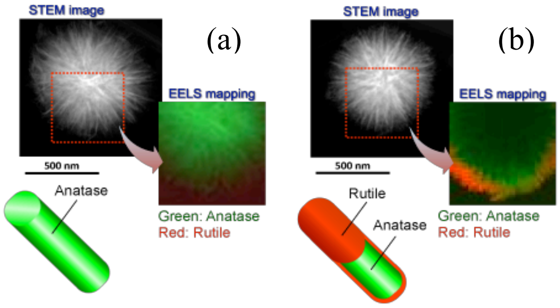

Fig. 2. STEM images and EELS maps of PTS calcined at (a) 500 and (b) 600 ºC.

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