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Antimony doped tin oxides and their composites with tin pyrophosphates as catalyst supports for oxygen evolution reaction in proton exchange membrane water electrolysis

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ABSTRACT

Proton exchange membrane water electrolyzers operating at typically 80 °C or at further elevated temperatures suffer from insufficient catalyst activity and durability. In this work, antimony doped tin oxide nanoparticles were synthesized and further doped with an inorganic proton conducting phase based on tin pyrophosphates as the catalyst support. The materials showed an overall conductivity of 0.57 S cm⁻¹ at 130 °C under the water vapor atmosphere with a contribution of the proton conduction. Using this composite support, iridium oxide nanoparticle catalysts were prepared and characterized in sulfuric and phosphoric acid electrolytes, showing much enhanced catalytic activity. Electrolyzer tests were conducted at both 80 °C with an Aquivion™ membrane and at 130 °C with a phosphoric acid doped Aquivion™ membrane. Significant improvement in the anodic kinetics was achieved on the composite supported catalysts at 130 °C although the electrolyzer cells showed higher ohmic resistance primarily from the membrane and catalyst layer. A durability test of electrolyzer cells was carried out at 130 °C under a current density of 400 mA cm⁻² in a period of up to 760 h, showing rather good stability of the system.

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1. Introduction

All long term visions about use of hydrogen as an energy carrier include water electrolysis [1]. Proton exchange membrane (PEM) water electrolysis has received much attention due to its higher current densities, energy efficiency and purity of the hydrogen product, as compared to the traditional alkaline electrolysis [2,3].

PEM water electrolyzers are generally based on per-fluorosulfonic acid (PFSA) type membranes for operation at typically 80 °C [4]. Elevating the temperature to above 100 °C has been proposed by Linkous et al. [5] and recently demonstrated with phosphoric acid doped Nafion® membranes [6]. Higher operational temperatures offer advantages for both thermodynamics and electrode kinetics. From an engineering point of view, heat recovery, thermal management and

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pressurization as well as the subsequent gas product compression would also benefit from elevated temperatures of operation. On the other hand, highly corrosion resistant materials are desirable for catalyst supports, gas diffusion layers and cell construction [7]. For this purpose, tantalum coated stainless steel felts have recently been prepared as gas diffusion layer materials for acidic steam PEM water electrolyzers, showing sufficient corrosion resistance and electronic conductivity [8].

The most demanding materials for the technology are anodic catalysts, which are typically based on precious metal oxides e.g. IrO_2 and RuO_2 . Great efforts are being made to enhance the catalytic activity of the precious metal oxide catalysts. One method is to disperse the precious metal nanoparticles on a support in order to maximize the specific surface area and hence the mass specific activity of the catalysts. To achieve effective dispersion of the catalyst nanoparticles and reduce the ohmic losses as well as mass transfer limitations inside an electrode catalyst layer, sufficient conductivity and high specific surface area with preferable pore-size distribution are among the basic requirements for catalyst supports. In addition, excellent chemical and electrochemical stability is also a must in order to accomplish the long-term stability and durability.

For application in fuel cells, high specific surface area carbon and their nanostructured analogs e.g. carbon nanotubes have been successfully used as catalyst supports [9]. These materials are, however, susceptible to the highly corrosive environment in water electrolyzers, especially under high anodic potentials. The stability and durability of the oxygen evolution reaction (OER) catalyst supports, in other words, are the primary challenge from materials science points of views. So far, the investigated materials are based on oxides and other ceramics including $\text{Ti}_n\text{O}_{2n-1}$ [10], TiC [11], SiC-Si [12], SnO_2 [13] and its commercial antimony doped form [14,15].

Among these, antimony doped tin oxide is a conducting oxide that has been used for a wide range of applications such as fuel cells [16], lithium-ion batteries [17,18], gas sensors [19], and others. Wu et al. [14] and Marshall et al. [15] have prepared RuO_2 and $\text{IrO}_2\text{-RuO}_2$ catalysts supported on the commercial antimony doped tin oxide. The activity towards the OER was found to increase and attributed to the promotion of the dispersion of active phase on the surface of the antimony doped tin oxide support and the resultant high specific catalytic activity. The authors, however, did not investigate the electrical conductivity of either antimony doped tin oxide or the antimony doped tin oxide supported $\text{IrO}_2/\text{RuO}_2$ catalysts.

Considering the electrical conductivity, as emphasized by Tunold et al. [20,21], a catalyst layer with a thickness of $10\ \mu\text{m}$ and a resistivity of $10\ \Omega\ \text{cm}$ would exhibit an ohmic loss of $10\ \text{mV}$ at a current density of $1\ \text{A}\ \text{cm}^{-2}$. This should be the minimum requirement for selection of catalyst supports. In addition to the demanded electronic conductivity in the catalyst layer of an electrolyzer electrode, the ionic, or specifically protonic, conductivity is in fact of higher significance to the electrode performance. In the studied OER catalysts neither the catalysts nor the supports have any protonic conductivity. Technically the proton transport in a catalyst layer is obtained by introducing an ionomeric phase into the

catalyst layers. The ionomers used are typically perfluorosulfonic acid polymers e.g. Nafion[®] in both fuel cells and water electrolyzers [6,22–24]. Due to the low intrinsic proton conductivity of the ionomers, as compared with the electronic conductivity, a high content is needed. This is however undesirable, as the ionomers are in general a dense phase with very low gas permeability [25]. The introduction of too large amounts of ionomers therefore result in decreases in the specific active area of catalysts, in the porosity and mass transportation as well as in the electronic conductivity and therefore in the overall conductivity of the catalyst layer.

Other proton conducting materials than ionomers are available from the recent development based on inorganic solid acids or acidic salts [26–29]. Of special interest are pyrophosphates e.g. SnP_2O_7 , which exhibits high conductivities ($>10^{-2}\ \text{S}\ \text{cm}^{-1}$) at temperatures of up to $300\ ^\circ\text{C}$ under non-humidified conditions [30–32]. In the present work, antimony doped tin oxide nanoparticles were first synthesized, onto which proton conducting pyrophosphates were introduced to give a composite catalyst support with mixed electronic and protonic conductivity. Based on the composite support, iridium oxide catalysts were prepared and characterized for the OER by electrochemical and electrolyzer tests.

2. Experimental

2.1. Preparation of catalyst supports

SnO_2 and antimony doped tin oxide nanoparticles were synthesized as follows. SnCl_4 ($0.13\ \text{mol}\ \text{L}^{-1}$, Aldrich) and citric acid (5 wt%, Aldrich) were first dissolved in distilled water for preparation of SnO_2 supports. In case of antimony doped tin oxide, a certain amount of SbCl_3 and SnCl_4 with varied Sb doping molar content (3, 5, 8 and 11 mol%) were dissolved in distilled water with addition of citric acid. Ammonia water (10 wt%, Aldrich) was then added to the solution to obtain a precipitate of $\text{Sn}(\text{OH})_4$ or a mixed hydroxide precipitate of Sn and Sb, which were subsequently filtered and washed with distilled water until the chloride residues completely disappeared. The precipitate was transferred to water, heated to $70\ ^\circ\text{C}$ and the pH was adjusted to 2 by addition of oxalic acid (30 wt%, Aldrich), then mixed with polyethyleneglycol (Aldrich) as dispersion agent and dried at $80\ ^\circ\text{C}$ in a vacuum oven for 12 h. The resulting powders were finally calcinated at $600\ ^\circ\text{C}$ for 1 h to obtain SnO_2 or antimony doped tin oxide powders.

As shown by the conductivity measurements, the antimony doped tin oxide with 5 mol% antimony had the highest electrical conductivity. In the following synthesis of composite support from oxides and phosphates as well as supported iridium oxide catalysts, only this composition of the antimony doped tin oxide (Sb, 5 mol%) was used and hereafter referred to as Sb- SnO_2 .

To prepare pure tin pyrophosphate (SnP_2O_7), SnO_2 prepared as described above was first mixed with 85 wt% H_3PO_4 (Aldrich) at $200\ ^\circ\text{C}$ under stirring until a viscous paste was obtained. The initial molar ratio of phosphorus to tin was 3. The paste was then heat treated in an alumina crucible at $600\ ^\circ\text{C}$ for 1 h. For preparation of composite support,

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