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Electrocatalytic activity of RuO_2 with varying structural water content for Hydrogen Evolution Reaction

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Ruthenium oxide (RuO_2) is a versatile oxide material in the application of electrochemical technologies such as oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and chlorine evolution reaction (CER) [1-4]. RuO_2 is the main active ingredient in the Dimensionally Stable Anodes (DSA®), one of the greatest technological breakthroughs of the past 50 years of electrocatalysts in chlor-alkali and chlorate industry as well as other associated arenas. The success of RuO_2 as excellent electrocatalyst mainly due to its low electrical resistivity of 35.2 μΩ.cm at room temperature, which is only order of two times higher when compared to metallic Ru [1]. Moreover, RuO_2 is known for its high chemical stability towards alkali and acids.

Hydrogen evolution through electrochemical process has received wide attention because of its importance in both fundamental and technological aspects. HER is the one of key component in water-alkali electrolyzer and aqueous NaCl electrolysis (chlor-alkali, chlorate) process. It is well known that above two process are high electrical energy consumption industries and more current loses are due to cathodic H_2 evolution [5]. In recent years, consideration of oxide materials as cathodes for HER gaining more attention when compare to yesteryears cathode materials of metal or metal alloys [1, 5]. RuO_2 and RuO_2 containing composite materials (Ni-P+RuO_2; Ni-P+TiO_2-RuO_2; TiO_2-RuO_2; IrO_2-RuO_2) are studied for HER reaction. It has been reported that RuO_2 has remarkable stability and not reduced to metallic Ru during HER reaction [1]. However, it was observed that the activity of RuO_2 increases during HER reaction and this activation was proved due to the intrinsic property of oxide materials (structural changes of RuO_2 rutile structure by insertion of hydrogen, preferentially in a-axis /a-a plane of rutile RuO_2) and roughness as well as wetting of oxide layer. A recent review by Over [1] on surface chemistry of RuO_2 in electrocatalysis towards HER highlighted various author attempts to understand the mechanism as well as structural aspects of RuO_2 for hydrogen evolution. However, the hydrous and crystalline RuO_2 performance towards HER is not known so far.

Hydrous ruthenium oxide or $RuO_2.xH_2O$; where structural water content, $x > 0.5$ to 2.0 has proven different electrochemical activity, as super capacitor, Cl_2 and O_2 evolution reaction when compared to crystalline RuO_2 (where x lies < 0.3). With x~0.5, RuO_2 is the best supercapacitor and minimum value of x containing RuO_2 is the stable electrode material for O_2 or Cl_2 evolution reaction [6-7]. Based on systematic investigation, it was proved that hydrous RuO_2 represents the nanocomposite consisting of rutile-like Nanocrystals (supports the electronic conduction) surrounded by structural water molecules (supports the proton conduction) [7]. It was reported that right combination of electronic and protonic conduction, which depends on the calcination temperature of RuO_2 is most obvious parameter to tune the electrochemically active RuO_2 for desired application [1]. However, such a study is not available so far on HER over RuO_2 with varying structural water molecules.

In this symposium, the results obtained over hydrous RuO_2 prepared through ion-exchange method at room temperature as well as calcined at different temperatures for HER are presented. The obtained HER results are evaluated with aid of structural characterization of hydrous and crystalline RuO_2. High Resolution TEM image of crystalline RuO_2 is illustrated in Figure 1 and distance between lattice fringes value indicates the rutile RuO_2 structure. Cyclic voltammogram of hydrous and crystalline RuO_2 for HER (inset in Figure 1) indicates that the electrochemical activity of RuO_2 towards HER also largely depend on its electronic and protonic conductivity.

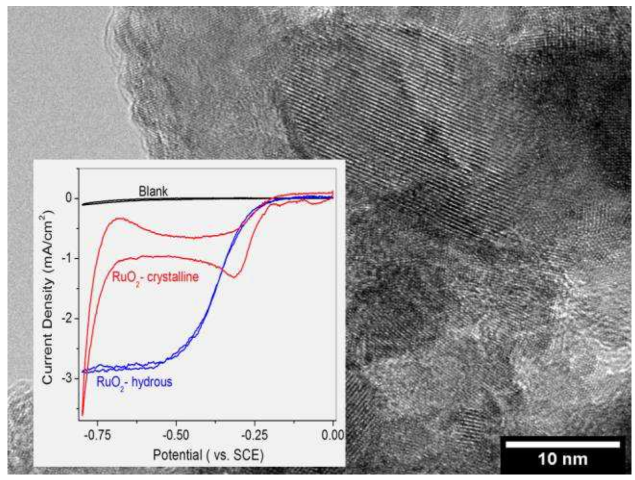

Figure 1. HRTEM image of crystalline RuO_2. Inset figure represents the cyclic voltammogram of hydrous and crystalline RuO_2 for HER in 1M Cl^- electrolyte of pH 2

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