

Electrochemical Activity of Non-precious Metal Tungsten Loaded Ceria cathodes for Polymer Electrolyte Fuel Cell Application

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Introduction

Polymer electrolyte fuel cells (PEFCs) have been developed as a power source for generating electricity using hydrogen and oxygen. In general, Pt is still the most practical cathode in PEFCs. However, the conventional Pt cathodes suffer significantly from high cost and low abundance. As a consequence of this, the development of non-precious metal electro-catalysts for oxygen reduction reaction (ORR) in PEFC is required. For this challenge, some non-precious metal ORR electro-catalysts such as transition metal chalcogenides [1], heat-treated nitrogen (N) containing Fe macrocyclic complexes [1], and N doped carbons [2] have been proposed. While those electro-catalysts would be promising candidates, the surface of those electro-catalysts is easily oxidized in cathodic condition and its activity would become low level during long term operation.

In our group, the Pt-CeO_x/carbon black (CB) has been developed as the ORR electrocatalyst in order to minimize the surface oxidation of Pt cathode and maximize the ORR activity on Pt in PEFCs operation condition [3-5]. The lowering of Pt surface oxidation and over-potential on Pt by Pt-CeO_x interaction was investigated by using in-situ XAFS analysis technique [6]. Based on this concept, the non-precious metal tungsten (W)-CeO_x cathodes were prepared for design of high quality non-precious metal ORR electro-catalysts with both high activity and long stability.

Experiment

Tungsten (W) powder was prepared by the reduction of WCl₆. WCl₆ particles were reduced by using the reducing agent Al based on the following equation (1).

$$\text{WCl}_6 + 2\text{Al} \rightarrow \text{W} + 2\text{AlCl}_3 \uparrow \quad (1)$$
 The mixed powder of WCl₆ and reducing agent Al was calcined at 600 °C for 1 h in a 10% H₂/He gas flow. The prepared W powder was rinsed into 1.0 M HCl aqueous solution. After filtration and drying, the dried W powder was mixed with the CeO₂ powder which was synthesized by hot ammonium carbonate precipitation method by using agate mortar. The home-made (HM) W and CeO₂ mixed powder was calcined at 500 °C for 1 h in a 10% H₂/He gas flow. The synthesized W-CeO_x was characterized using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses. The cathode properties of W (HM) and W-CeO_x cathodes were examined by cyclic voltammetry (CV) and voltammetry on Glassy Carbon (GC) electrode in 0.1 M KOH aqueous solution. To conclude the interaction between W and CeO_x in the interface of electro-catalysts, the structure simulation of the oxygen defect cluster was performed by using the general utility lattice program (GULP).

Results and discussion

To examine the electrochemical property of W-CeO_x, the CV on GC electrode in 0.1 M KOH aqueous solution was performed using both W and W-CeO_x electrodes as shown in Fig. 1(a, b). All of the voltammograms in Fig. 1(a, b) were examined after 30 cyclic sweeps. In the observed CV recorded from W sample, the mid level of CV observed for W was shifted into positive current region. Namely, the anodic current was clearly observed in forward sweep while it was hard to observe the cathodic current in back sweep as demonstrated in Fig. 1(a). This shift of CV indicates that the observed CV was affected by the semi-conducting property of W-oxide surface. The surface of W would be oxidized during CV measurement. Alternatively, the mid level of CV profile observed for W-CeO_x is located at 0 mA as well as Au electrode. It means that both anodic current and cathodic current were clearly observed in forward and back sweeps in Fig. 1(b). This data clearly indicates that the surface oxidation of W metal is inhibited by the formation of the W-CeO_x hetero-interface as well as Pt-CeO_x/CB [2, 3].

In the presentation, the characterization data and ORR activities of W-CeO_x/CNT (Carbon Nano Tube) will be introduced. Also, the simulation result about the oxygen defect cluster in W-CeO_x hetero-interface will be presented to clarify the role of metal-oxide interface on ORR activities.

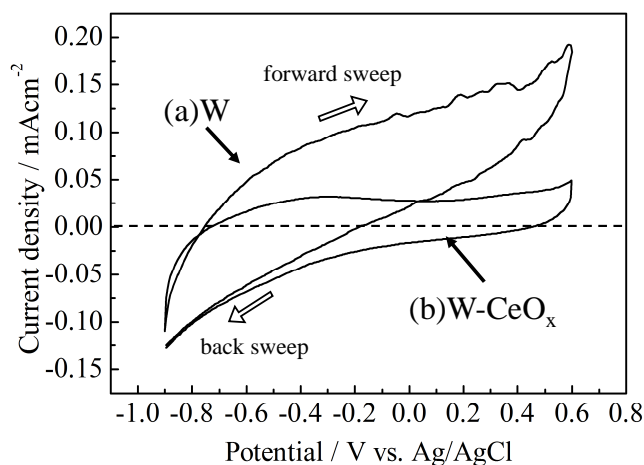


Fig. 1 Cyclic voltammograms observed for W(HM)(a) and W-CeO_x(b) on GC electrode into N₂ saturated 0.1 M KOH aqueous solution.

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