

Study of Alternative Oxygen Reduction Electrocatalyst for Pt Based on Transition Metal Chalcogenides

Yukiyoshi Ueno and Hirofumi Iisaka

Toyota Motor Corporation

Kazuhiko Dohmae

Toyota Central R&D Labs., Incorporation

Copyright © 2008 SAE International

ABSTRACT

The development of an alternative oxygen reduction electrocatalyst to platinum based electrocatalysts is critical for practical use of the polymer electrolyte membrane fuel cell (PEMFC). Transition metal sulfide chalcogenides have recently been reported as a possible candidate for Pt replacement. Our work focused on chalcogenides composed of ruthenium, molybdenum, and sulfur (RuMoS). We elucidate the factors affecting electrocatalytic activity of carbon supported $Ru_xMo_yS_z$ catalyst. This was demonstrated through a correlation of oxygen reduction reaction (ORR) activity of the catalysts with structural changes resulting from designed changes in sulfur composition in the catalysts.

INTRODUCTION

In recent years, there has been increasing interest in the development PEMFC-s as a future power train of the automobile due to its high efficiency and use at low temperature. However the practicality of this technology is challenged by high cost mainly from Pt (currently the best catalyst for ORR) based electrocatalysts and low durability due to the highly acidic environment of the PEMFC. There is great interest in Pt-free alternative oxygen reduction electrocatalysts for PEMFC application as a strategy to reduce cost. Some of the most popular candidate alternatives are, porphyrins (which have a central active metal), metal carbides (which have a similar electronic structure to Pt), and chalcogenides (as the transition metal sulfide). Activity gains with these catalysts are not well understood especially through the relationship between catalyst structure and ORR activity. We consider chalcogenide catalysts focusing on those composed of ruthenium, molybdenum, and sulfur (RuMoS) because they have been shown to have ORR activity and good stability in acid media. We clarify the factors that influence ORR activity $Ru_xMo_yS_z/C$ catalyst through a correlation of ORR activity results with structural changes resulting from changes in active metal and sulfur composition of the catalysts. In this paper we present and discuss results from analytical

measurement techniques such as X-ray Diffraction (XRD), Transmission Electron Microscope (TEM), Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Photoelectron Spectroscopy (XPS). Results from these analytical techniques provided structural information on the $Ru_xMo_yS_z/C$ catalysts, which were combined with ORR activity results from Rotating Disk Electrode (RDE) measurements. A proposed mechanism for ORR on these catalysts is also presented.

MAIN SECTION

1.Experimental

1-1.Catalyst preparation Carbon-supported RuMoS of various compositions were prepared by refluxing the respective carbonyls $Ru_3(CO)_{12}$ (Strem Chemicals), $Mo(CO)_6$ (Acros Organics) together with various amounts of sulfur in the presence of carbon (Ketjen Black EC) in xylene for 20 hours under argon. Xylene was used for deaeration beforehand. The reaction mixture was filtered and washed with acetone and dried in an oven under vacuum at 100°C overnight after cooling. Finally, the products were heat treated at 350°C for 2 hours under vacuum. The heat treatment was carried out with a cylindrical titanium tube. The contents of each reagent of the catalysts can be seen in Table 1. A flow chart showing the process can be seen in Fig.1

Table1. Compositions of the prepared catalysts

Composition	Ru(mg)	Mo(mg)	S(mg)	S(mol%)
Ru5MoS1.5	796	155	76	20
Ru5MoS3.5	796	155	176	37
Ru5MoS5	796	155	252	45
Ru5MoS7.5	796	155	378	56
Ru5MoS15	796	155	756	71
RuS	796	0	206	45
MoS	0	796	213	45
Ru	445	0	0	0

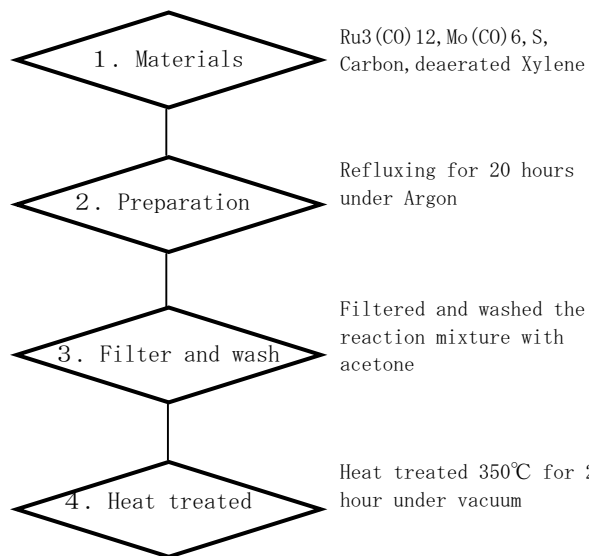


Fig.1 Catalyst preparation process

1-2.Catalyst Evaluation and Analysis ORR activity evaluations were carried out by RDE. All catalyst evaluation experiments were performed in 0.1 N HClO₄. The working, reference and counter electrodes were glassy carbon, hydrogen and Pt wire respectively. The electrodes were prepared by dropping 5 μ l of catalyst ink on a glassy carbon disk. The catalyst inks were prepared by adding homogeneously-distributed catalyst in a solution containing ethanol and a small amount of Nafion. TEM-measurements were carried out at 300 keV in the acceleration voltage. The X-ray absorption experiments were carried out at the BL01B1 beam line at Spring-8 equipped with an ionchanba. The higher harmonic radiation was removed at a photon energy of 22120 eV (Ru-K edge). XPS measurements were carried out with ULVAC system. Note that ORR activity comparisons are made for 0.7 V and 1600 rpm.

2.Results and Discussion

2-1 Analysis of catalyst structure- The analytical techniques used to characterize the catalysts are summarized in Table 2.

Table2. Characterization of catalysts

Method	Technique	Measurement	Purpose
Analytical (Structur)	XRD	Crystalline state	Determine existence of metallic crystal
	TEM	Particle image	Determine particle size
		Crystalline state	Determine existence of metallic crystal
	EXAFS	Coordination	Determine atom coordination
Electro chemical (Activity)	RDE	XPS	Identify elements on surface of catalyst
		ORR activity	Identify active metal in catalyst

2-1-1.Electrochemical characterization In order to clarify the catalyst active structure, it is necessary to identify the active metal. Fig. 2 shows the ORR activity for Ru₅MoS₅, RuS, MoS. All catalyst with Ru showed activity towards ORR therefore we conclude that the active metal is Ru. And, we measured the number of the electron reduction of Ru₅MoS₅ by using Koutecky-Levich equation. There, we obtained that the number were 3.7. So, we conclude that Ru₅MoS₅ is nearly 4-electron reduction catalysts.

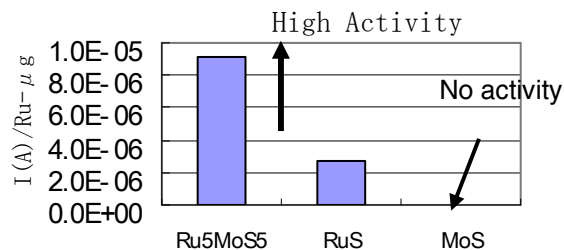


Fig2. RDE measurements of catalysts with different metal content

2-1-2. XRD Results Fig. 3 shows XRD results on the Ru₅MoS₅ catalyst. The existence of the Ru metal is confirmed from the peak and intensity

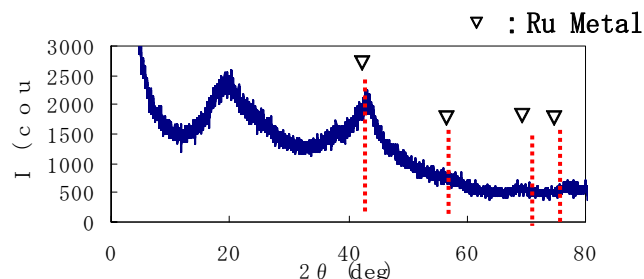


Fig. 3. XRD results on Ru₅MoS₅ catalysts

2-1-3. TEM measurements- Fig. 4a and b show TEM images of carbon supported chalcogenide with 45 mol% sulfur content. The chalcogenide in Fig. 4a have very small particles of about 3–4 nm and a crystal grating on the carbon. Ru was identified as the metal because the crystal grating was equal to the Ru metal by fourier transform. There was no evidence of Mo and S bonding with the Ru metal.

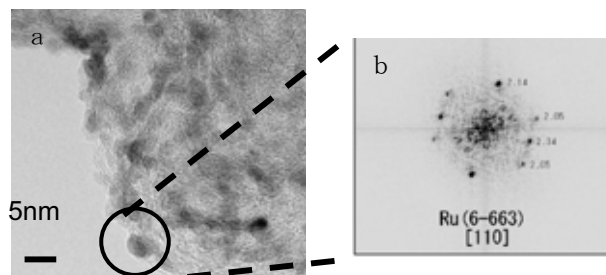


Fig. 4(a) TEM image of of Ru₅MoS₅
(b) Fourier transform of Ru₅MoS₅