# 폴리올 방법에 의한 산소 환원 반응용 RuSe/C 촉매 개발

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# RuSe/C catalysts preparation by polyol method for oxygen reduction reaction

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## Introduction

Fuel cell is one of the best candidates for clean energy. However, there are many problems for commercialization such as fuel cell prize, durability higher power density. Especially platinum catalyst is main reason of fuel cell prize. Then, non-platinum catalysts has been studied by many researchers. Palladium-transition metal[1], active carbon[2], and Ruthenium-chalcogen metal[3,4] are suggested as substitutions for platinum. Among them, RuSe catalysts show good activity for oxygen reduction reaction(ORR) and high methanol tolerance. A combination of Ru with Se at a proper Ru:Se ratio increases the ORR activity, compared to Ru alone, which is attributed to function of Se as oxygen adsorption site and electron bridge [4]. In this study, porous carbon supported RuSe catalysts are prepared by polyol method and studied to investigate the influence of selenium on the catalytic activity of the catalyst.

## Experiment

We prepared RuSe/C 60wt% catalysts with different Se ratio (5, 10, 15, 20, 30, 50 mol%). $RuCl_3$, Ru(acac) and $SeCl_3$ were used as metal precursors and EG(ethylene glycol) was selected as reducer. After dissolving the precursors in EG, the mixture was heated to below solvent boiling temperature and kept under refluxing condition for 4h. Then, catalysts were cleaned by water and ethanol. Electrochemical studies were performed with Rotating Disk Electrode (RDE) equipped with a platinum wire counter electrode, Ag/AgCl reference electrode (BAS Co., Ltd., MF-5B) and the working electrode. Rotating machine is RDE-1(Bioanalytical Systems Inc.). All potentials shown in this paper are converted to the reversible hydrogen electrode (RHE) scale. Cyclic Voltammetry(CV) was measured at a scan rate 15mV/s of 1M $HClO_4$ which was purged by $N_2$.The ORR was measured

by potential sweep of a 1M $HClO_4$ solution which was concentrated by oxygen at a scan rate of 5mV/s. Methanol tolerance tests were measured at same condition except the electrolyte containing methanol.

XRD patterns of the catalysts were obtained with a D/MAX-ⅢC diffractometer (Rigaku Co.) using CuKa radiation. For XPS measurements, the catalysts were palletized and measured at 8.4kV, 14mA, Mg Kα radiation.

**Results and discussions**

Fig.1. shows XRD patterns of the prepared catalysts. The RuSe catalysts showed clear peak and peaks mean that Ru exist as metal formation in bulk system. All catalysts prepared by polyol method have much higher portion of Ru metal than Ru oxide. Then each particle size of catalysts is 5.6, 3.9, 3.6, 4.1 and 4.6 nm for the Se 5, 10, 15, 20 and 25 mol%.

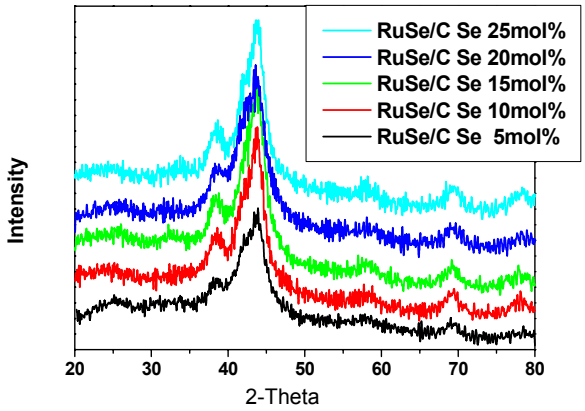



Fig. 1. XRD patterns of the RuSe/C catalysts (Se: 5, 10, 15, 20 ,25 mol%).

Se modified Ru catalysts examined by CV and results are presented in Fig. 2. Increasing Se contents, Ru oxidation voltage are decreased. In case of Se 5mol% catalysts, Ru are largely oxidized from between 0.2~0.3V. Over 10mol% Se contents, however, Ru oxidation currents are significantly decreased.

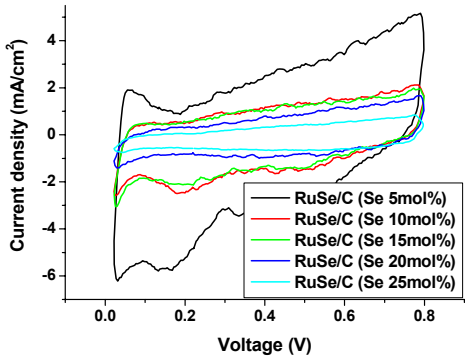



Fig. 2. CV test of RuSe/C catalysts (Se : 5, 10, 15, 20 25 mol%).

Fig. 3. shows ORR results of RuSe/C catalysts(Se: 5, 10, 15, 20, 25 mol%) and Pt/C 60wt%(E-TEK). Current densities at 0.7 V were 1.245, 1.558, 1.739, 1.856, 0.932 and 2.25 mA/cm$^2$ for 5, 10, 15, 20, 25 Se mol% and Pt/C catalysts, respectively. 20mol% Se containing catalyst shows best activity among Se modified Ru catalysts and has over 80% activity of Pt/C 60wt% (E-TEK).

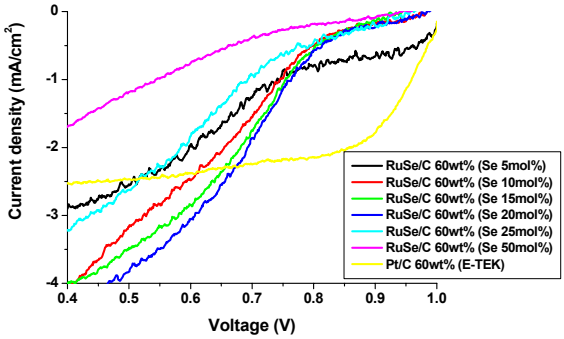
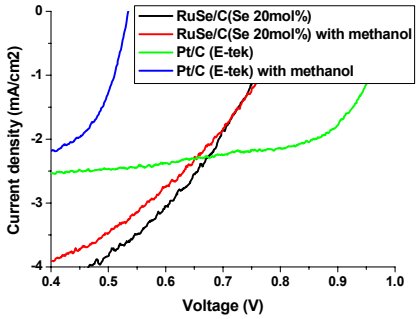


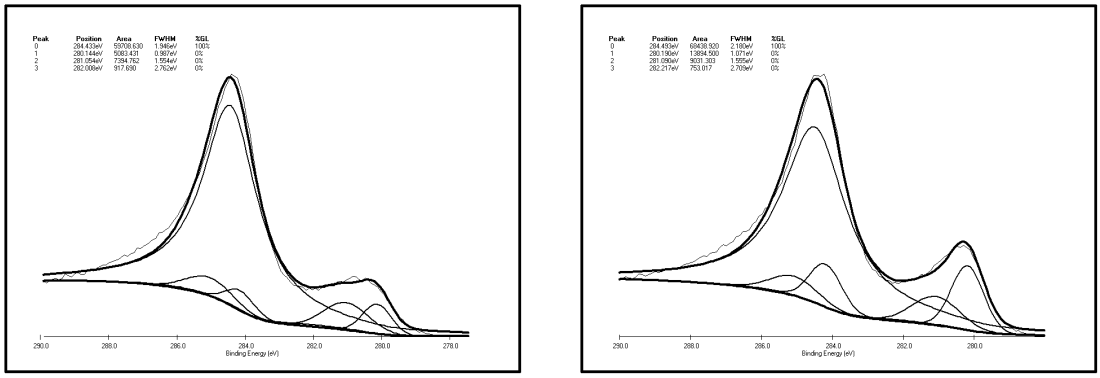

Fig. 3. ORR results of the RuSe/C catalysts (Se: 5, 10, 15, 20 ,25 mol%) and Pt/C 60wt% (E-TEK).

Fig. 4. displays methanol tolerance property of catalysts. Se modified Ru catalysts (Se: 20mol%) shows much higher methanol tolerance property than Pt catalysts. High methanol tolerance property is one of the important condition for cathode catalysts of DMFC.




Fig, 4. Methanol tolerance results of RuSe/C (Se 20mol%) and Pt/C 60wt% (E-TEK)

XPS results of RuSe/C (Se: 5mol%, 20mol%) catalysts for $Ru3_d$ are shown in Fig. 5. Carbon 1S(284.5 eV), Ru metal (180.1 eV) and Ru oxide (181 eV) peaks are simulated by XPS peak 4.1 to separate them. In the case of Se 5mol% catalysts, ratio of Ru metal and Ru oxide is 41:59 in surface of catalysts. Ratio of Ru metal and Ru oxide is 60.6:39.4 in the Se 20mol% catalysts. This result means that amounts of Ru metal are increased with increase of Se contents. Ru metal are more active than Ru oxide for oxygen reduction[4]. This result has consensus with ORR results.




(a) (b)

Fig. 5. XPS measurement results for Ru 3d of (a)RuSe/C (Se 5mol%) and (b) RuSe/C (Se 20mol%)

**Conclusions**

Various composition of RuSe/C catalysts were prepared by polyol method for oxygen reduction. Se 20mol% catalyst has the best activity for ORR. Adding Selenium, Ru oxidized voltage is decreased and amounts of Ru metal are increased in the surface of catalysts. Se 20 mol% catalyst shows over 80% activity with Pt/C 60wt% (E-tek) catalyst for oxygen reduction.

**References**

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