The ruthenium-based chalcogenide are widely investigated as promising non-platinum catalysts, due to its high catalytic activity and stability towards oxygen reduction reaction (ORR) in H₂SO₄ electrolyte solution [1, 2]. The reported results have shown that the catalytic activity of Ru and Ru₃Se cluster compounds is still low compared to that of platinum, however, the catalytic performances of RuₓM₄Se₅ (M=Fe, Cr, Mo, W) bimetallic chalcogenide to the ORR can be improved by the incorporation of Ru and Se into a second transition metal [3, 4].

In the present work, the preparation and catalytic properties of RuCrMoSe trimetallic chalcogenide as cathode oxygen reduction catalyst is presented. The novel catalyst was synthesized by decarbonylation of the transition metal carbonyl compounds in 1, 6-hexanediol solvent containing dissolved selenium under refluxing conditions. The electrochemical experiments were completed in a single three-electrode test cell at 25 °C. The rotating disk electrode (RDE), platinum wire and Hg/H₂SO₄ electrode was used as the work, counter and reference electrode, respectively.

The XRD pattern of the as-synthesized RuCrMoSe catalyst is shown in Fig. 1. The sample maintained the hexagonal structure of Ru₃ cluster as the main phase and formed an amorphous phase. The catalyst powder consisted of agglomerates of nanometric size (95~170 nm) particles. Polarization curves of the ORR on the catalyst were recorded by the LSV technique with a scanning rate of 10 mV s⁻¹ from the open circuit potential to 0.05 V (vs. NHE) at rotating speeds of 100, 200, 400, 900, 1600 and 2500 r min⁻¹ in O₂-saturated 0.5 mol dm⁻³ H₂SO₄ solution. The dependence of the cathodic current density on the potential and the rotation rate is shown in Fig. 2. Large cathodic current density towards the ORR could be obtained in the oxygen saturated electrolyte, indicating that the catalyst had high catalytic activity for the ORR. It can also be seen that the current density of oxygen reduction on the catalyst increases with rising rotation speeds due to the increase of oxygen molecule diffusion through the GC electrode surface. The catalyst shows a higher current density than that of the RuₓCrₓSe₅ catalyst, indicating that the catalytic activity of the RuₓCrₓSe₅ clusters to the ORR can be enhanced by adding Mo element. The RuCrMoSe cluster compound demonstrated significant electrocatalytic activity towards the ORR, showing an open circuit potential (OCP) of 0.91 V (vs. NHE) in 0.5 mol/L H₂SO₄ electrolyte saturated with oxygen at 25°C. The kinetic parameters, the transfer coefficient, Tafel slope and exchange current density, are determined to be 0.42, 142 mV and 4.22×10⁻⁴ mA cm⁻² from the mass-transfer corrected Tafel plot, respectively. To investigate the electrochemical stability of the catalyst in the acid solution during oxygen reduction, chronoamperometry was carried out during 1000 s at fixed potential of -0.2 V [5]. It was also clear that the decay rate of catalytic activity was calculated to be 2.09% and 1.21% for the prepared catalyst and the commercial platinum catalyst, respectively. The result suggested that the electrochemical stability of the RuCrMoSe catalyst should be further improved, compared with the commercial platinum catalyst. The better electrocatalytic performances of the RuCrMoSe trimetallic chalcogenide towards the ORR can be attributed to the synergistic effect of between Ru element and the other transition metals in the catalyst.

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References