Nanocrystalline lead ruthenium pyrochlore as oxygen reduction electrode

V Raghuvender, Keshav Kumar & B Viswanathan*
Department of Chemistry, Indian Institute of Technology, Madras, Chennai 600 036, India

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The synthesis of nanocrystalline Pb-Ru pyrochlore of composition \( \text{Pb}_2\text{Ru}_{1-x}\text{Pb}_{0.7}\text{O}_{2.8} \) was studied for the potential usage in the electrochemical reduction of oxygen. The nanocrystalline pyrochlore was synthesized by reverse micellar method. The single phase oxide formation and crystallite size determination (1-20 nm) were carried out using X-ray diffraction and transmission electron microscopic studies respectively. The electrocatalytic activity for oxygen reduction and its comparison with the oxide prepared by conventional ceramic method are also reported here.

The electrochemical reduction of molecular oxygen at the electrode surface is important, especially in electrochemical energy devices such as metal air batteries and direct hydrocarbon/air fuel cells. In most of these devices, especially in fuel cells, the oxygen reduction is carried out using Pt metal supported carbon electrodes. At high potentials, the formation of absorbed species on the platinum surface inhibits the oxygen reduction reaction and hence results in performance loss. Studies for exploiting metal oxides as cathodes for the reduction of oxygen have already been carried out since these materials can be expected to provide reversible pathway for oxygen reaction.

The development of less expensive oxide electrocatalyst for the reduction of oxygen at lower potentials can have major economic consequences. The Pb-Ru pyrochlore has been first identified by Horowitz et al. as an active electrocatalyst for oxygen reduction whose efficiency is considered to be comparable to that of the noble metals in alkaline medium. This material is also known to be stable in acids for several days. The nature of oxide surface generally depends on the pH of the electrolyte and hence the nature of active sites also change with pH. The \( \text{AB}_2\text{O}_3\text{O}' \) type pyrochlore has two types of oxygen; the O' oxygen bonded to both A and B cation, whereas the O oxygen bonded to only A cations. The active oxide sites responsible for the rate determining step of the oxygen reduction reaction (ORR) in alkaline and acid media is O' and O sites respectively.

The activity of \( \text{Pb}_2\text{Ru}_{1-x}\text{Pb}_{0.7}\text{O}_{2.8} \) for oxygen reduction depends on the Pb content in the B sub-lattice. The maximum activity is achieved for the composition \( \text{Pb}_2\text{Ru}_{1-x}\text{Pb}_{0.8} \text{O}_{2.8} \). The Pb-Ru pyrochlore prepared by conventional ceramic method shows activity for oxygen reduction but it is quite low. The enhancement in the activity for oxygen reduction is noticed when Pb-Ru pyrochlore was dispersed on the Vulcan XC 72 R carbon.

Nanostructured materials are of great importance as they find applications in the fields of optics, electronics, mechanics and catalysis. In catalysis, they offer unique size-dependent property, a large surface to volume ratio and unusual chemical/electronic synergistic effect from an ultrahigh component dispersion. Nanocrystalline materials differ greatly from the conventional materials because they have large interfacial area where the atoms appear in unsaturated coordination and have many dangling bonds. This structure must have a special influence on the properties of such materials. There are several ways of preparing the nanocrystalline oxides such as use of spherulite technology, using polymer matrix such as polyethylene glycol-gel and stearic acid-sol and reverse microemulsion method, RME.

Colloidal assemblies such as reverse micelles/water in oil microemulsions seem to be good candidates for growing nanoparticles. These surfactant stabilized reverse micelles (called microemulsions) offer a unique environment for the formation of nanosized oxide particles. They not only act as nanoreactors but also act as steric stabilizers to inhibit the crystal growth. Reverse microemulsion consists of nanometer-sized water droplets dispersed in oil phase and stabilized by the surfactant molecules accumulated at the oil-water interface. The dispersed water droplets act as nanoreactors for the formation of...
nanosized inorganic particles. The size of the particles is of the order of the size of water droplets. Size of the particles can be controlled by varying the composition of microemulsion. The main advantage of this method is that the preparation method is soft, simple and does not require extreme conditions like pressure and temperature. Different types of particles such as LiCoO₂, Barium Hexaluminate, Calcium phosphate, Ag nanoparticles were prepared by the reverse micelle method. The best of our knowledge, no prior work on Pb-Ru pyrochlore synthesis by the reverse micelle technique has been reported. The synthesis of nanosized Pb-Ru pyrochlore of composition Pb₁₋ₓRuₓPb₀ₓO₂₋ₓ by reverse microemulsion method, its characterization by XRD, TEM, and its electrocatalytic activity for oxygen reduction, are reported here.

Experimental Procedure

The microemulsions were prepared by mixing aqueous solutions of the stoichiometric amounts of lead nitrate (s.d. Fine-chem Ltd.) and ruthenium chloride trihydrate or aqueous solution of KOH (E-Merck) with 0.1 M AOT (sodium dioctyl sulfosuccinate)/n-heptane. The AOT and n-heptane was obtained from Loba Chemie and CDH respectively. The reagents were used as received. In both microemulsions, the water to AOT ratio is maintained at 15, which corresponds to the water droplet size 6 nm. In the microemulsion I, the molar concentration of lead nitrate and ruthenium chloride were 8x10⁻⁴ M and 7.9x10⁻⁴ M respectively. In the microemulsion II, the molar concentration of KOH was 5.9x10⁻⁵ M. To facilitate the mixing of metal salt solution into the oil phase, ultrasonication was carried out for 10 min. The two microemulsions were mixed together with vigorous stirring at room temperature for 2 h which is sufficient to complete the reaction. To recover the particles from the micelles, acetone was added to break the surfactant molecules. The sedimented particles were washed with acetone and water successively to remove the surfactant molecules and sodium ions. The washed Pb-Ru pyrochlore particles were dried in air oven maintained at 120°C for 2 h followed by calcination at 500°C for 2 h in air.

The nanocrystalline oxide was characterized using X-ray diffraction pattern obtained with a Rigaku instrument using Fe-filtered CoKα radiation. The nanocrystallite size was determined using Transmission Electron Microscopy (TEM) with Philips CM12/STEM.

The electrochemical reduction of oxygen was carried out using cyclic voltammetry (Potentiocran Wenking Model POS 73). The reference and counter electrodes used in the present study were saturated Ag/AgCl and Pt (1.5 cm² area), respectively. The oxygen reduction was carried out in 1 M H₂SO₄ solution and purging oxygen gas. The electrode was prepared as follows, 20 mg of oxide was dispersed in 0.5 ml distilled water and ultrasonicated for 30 min. From the dispersion, 20 μL dispersion was taken on the glassy carbon surface and dried in air followed by the addition of 5 μL of 5% Nafion solution as binder. The amount of the Pb-Ru oxide taken on the glassy carbon substrate is around 200 μg.

Results and Discussion

Particle recovery—Initially when the microemulsions were mixed, the emulsion was clear. After few seconds, emulsion became turbid because of the formation of the particles. Because of the high viscosity of the microemulsion, the particles formed on the reverse micelles were not sedimented at the bottom of the beaker. The particles were released on addition of acetone and settled down as black mass at bottom of the beaker.

Characterization by X-ray diffraction—The X-ray diffraction pattern observed for the Pb-Ru oxide prepared by the RME confirmed the formation of pyrochlore structure and is shown in Fig. 1. The pattern has been found to match well with that of the standard pattern of Pb-Ru pyrochlore reported in the JCPDS standard file No. 34-472. The XRD peaks in Fig. 1 are characteristically broader than normally obtained for large crystallites which is expected for nanosized crystallites.

Transmission Electron Microscopy—Transmission electron micrographs of Pb-Ru pyrochlore taken in different regions recovered from the microemulsion are shown in Fig. 2. The TEM pictures show the ultrafine dispersion of nanosized oxide particles. The overall particle size of the pyrochlore oxide ranges from 1-20 nm. In Fig. 2a, the particle sizes have been found to be in the range 1-4 nm. It implies that the

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Fig.1—XRD pattern for the Pb₁₋ₓRuₓPb₀ₓO₂₋ₓ nanoparticles.
size of the oxide particles formed in the microemulsion is of the same order of the water droplet size. The morphology of the oxide particles shown in Fig. 2b also shows particle sizes >15 nm. It means that the size of the particles grows during the calcination process at 500°C for 2 h; or during the intermicellar exchange, the particle grows to a size which may be greater than that of size of the water droplet. We also observed the formation of filament type particles (Fig. 2c) which has been reported by other researchers. This may be due to the formation of different liquid crystalline phases of the microemulsion at higher water contents.

Electrochemical reduction of oxygen—The cyclic voltammogram obtained for the electrochemical reduction of oxygen using nanocrystalline Pb-Ru pyrochlore prepared by RME as cathode is shown in Fig. 3a. The differences in the voltammograms obtained in the presence of oxygen and with that of the deaerated solution, show that the oxygen reduction reaction is taking place. The current density at -0.6 V vs Ag/AgCl provides a measure of activity. The activity decreases on deaerating the electrolyte with N₂ gas. The activity for oxygen reduction has
been found to be enhanced (approximately 8-9 times) in the case of Pb-Ru pyrochlore prepared by RME compared to that of the conventional ceramic method (the corresponding cyclic voltammogram is shown in Fig. 3b). Moreover, a shift of reduction onset potential by 50 mV for the nanocrystalline Pb-Ru pyrochlore has been observed. This suggests that the particle size is playing a major role in the activity and the onset potential to some extent for the oxygen reduction.

Conclusions
Nanoparticles of Pb$_3$Ru$_{1-x}$Pb$_{0.05}$O$_{2.8}$ were prepared using reverse microemulsion method. The X-ray diffraction confirms the formation of pyrochlore phase. The TEM measurements confirm the particle diameter range 1-20 nm. The nanosized Pb-Ru pyrochlore shows nine times higher activity for oxygen reduction compared to that of the one prepared by the conventional ceramic method.

References