Selenourea-assisted synthesis of selenium-modified iridium catalysts: evaluation of their activity toward reduction of oxygen

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A B S T R A C T

Carbon-supported selenium-modified iridium nanoparticles have been synthesized using $IrCl_3$ and selenourea serving as a precursor of selenium and nitrogen atoms. Here nanostructured iridium is chosen as model base metal for fundamental catalytic considerations because it exhibits interfacial properties resembling both platinum and ruthenium. The systems' electrocatalytic properties have been studied in sulfuric acid electrolyte toward reduction of oxygen and formation of hydrogen peroxide intermediate in comparison to bare iridium and platinum catalysts. To get insight into the reaction dynamics and mechanisms, such electrochemical diagnostic techniques as cyclic voltammetry and rotating ring-disk electrode voltammetry have been considered. To mimic operation of catalysts in real fuel cells, additional experiments utilizing gas diffusion electrode have also been performed. Materials are subjected to surface analytical, structural and microscopic characterization using X-ray photoelectron (XPS), fluorescence (EDX), and diffraction (XRD) methods as well as transmission and scanning electron microscopies. At low (optimum) coverages of selenium on surfaces of iridium nanoparticles, the reduction of oxygen tends to proceed at more positive potentials in comparison to bare iridium under analogous conditions. Apparently, strong affinity of bare iridium to form oxo groups on its surface (known as inhibiting oxygen reduction) is largely suppressed in presence of selenium or nitrogen atoms. But the optimum selenium-modified iridium system produces somewhat higher amounts of the hydrogen peroxide intermediate presumably due to partial physical blocking of iridium (metal and metal oxo) sites (that would otherwise be active toward the reduction of the H_2O_2 intermediate). High tolerance (during reduction of oxygen) of the optimum Ir-based catalyst (functionalized using selenourea) to the parasitic (e.g. in polymer membrane fuel cells) simultaneous oxidation of organic fuels (e.g. methanol or ethanol) should be mentioned as well.

1. Introduction

Despite significant progress in the area of the electrocatalytic reduction of oxygen, its efficient electroreduction still remains a fundamental problem, particularly, when it comes to potential applications in low-temperature fuel cells utilizing organic fuels such as methanol, ethanol or, more recently, formic acid. Possibility of their crossover through the membrane leading to depolarization of a cathode in a fuel cell, typically results in lower efficiencies of devices utilizing organic fuels in comparison to hydrogen. It is well established that, during oxygen reduction, typical platinum-based catalysts suffer not only from the lack of (or low) tolerance to the presence of organic fuels (methanol, ethanol or formic acid), but they are also prone to poisoning by their oxidation intermediate products, particularly CO-type adsorbates [1–6]. Fundamental research is required for the development of alternative materials (as cathodes in fuel cells) with both high activity and selectivity. The most promising examples included systems utilizing platinum alloys with other metals [7,8], transition metal macrocycles and their synthetic analogs (mainly with cobalt or iron ionic sites) [9,10] and metal chalcogenides of certain noble (Ru, Ir, Rh) [11–17] as well as non-noble (Co, Fe, Ni) [18,19] metals. Many publications concerned ruthenium-selenium catalysts [11–14,20–22], highly active Ru-based chelates [23,24] and, later, carbon supported ruthenium-selenium nitrogen-chelated catalysts [25,26], where one compound, namely selenourea, is used as the precursor of selenium and nitrogen. The aim of such approach was to combine the features of Ru-Se and Ru-N compounds.

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In the present work, we have concentrated on iridium as model noble metal exhibiting properties resembling platinum, particularly with respect to hydrogen adsorption capabilities, and ruthenium in terms of the high affinity to form oxygen containing species at low potentials [27,28]. It should be remembered, however, that iridium (although much more expensive) is much more resistive (relative to ruthenium) to corrosion (and dissolution) upon application of positive potentials typically appearing during reduction of oxygen in a fuel cell. We present here the results concerning electrochemical and electrocatalytic properties of iridium-based catalysts modified with selenium (from selenourea). It is apparent from the rotating ring-disk electrode (RRDE) diagnostic experiments that reduction of oxygen proceeds at more positive potentials following modification of iridium with the optimum (low) amount of selenium (from selenourea). Under such conditions, the respective system is characterized by higher heterogeneous rate constants (relative to that found at bare iridium of the same loading) at such potentials as 0.5 V, or even higher. The reduction of oxygen has been found to be selective and tolerant to the presence of organic fuels such as methanol or ethanol (but not formic acid). The system's tolerance to alcohols (e.g. crossing over in a fuel cell from the anode to cathode compartment) may also be of potential importance to the development of mixed-reactant (membraneless) fuel cells. Because of the high cost of iridium-based catalysts, the proposed systems are not for direct application in fuel cells. Therefore, the present research is on the intentionally modified noble-metal nanostructured-catalysts which are of fundamental importance to the electrochemical energy conversion.

2. Experimental

All chemicals were commercial materials of the highest available purity. H_2SO_4, HCl, HNO_3, K_2SO_4, methanol, ethanol, formic acid, 2-propanol and $K_3[Fe(CN)_6]$ were obtained from POCh (Poland), the solution of 5% Nafion-1100, selenourea (abbreviated as *SeU*) from Sigma-Aldrich, $IrCl_3$&903;xH_2O from Alfa Aesar (Germany), Vulcan XC-72R (C) from Cabot (USA), hydrogen peroxide 30% from Chempur (Poland); and nitrogen, oxygen and the mixture of argon (99%) and hydrogen (1%) gases (purity 99.999%) were from Air Products (Poland). Vulcan XC-72R was purified and activated in HCl and HNO_3 according to the procedure described in the literature [29]. The solutions were prepared from doubly-distilled and subsequently-deionized (Millipore Milli-Q) water. All electrochemical experiments were conducted at room temperature, $22 \pm 2\,°C$.

Selenourea-assisted synthesis of carbon-supported selenium-modified iridium (IrSeU/C) catalysts (with final Ir loading at the level of 10 and 20% w/w) was achieved in a manner analogous to the approach described in our preliminary paper [25]. The suspension of carbon support and solutions of precursors (selenourea, *SeU*, and $IrCl_3 \cdot xH_2O$ with the proper amount of salts in 2-propanol) were independently sonicated for 30 min to homogenize and dissolve them. Then they were mixed together and further sonicated for 30 min. Finally argon was passed through the solution, and the mixture was refluxed for 2 h. After drying at room temperature, the powders of precursor blends were annealed at $400\,°C$ for 2 h in the mixture of $H_2(1\%)/Ar(99\%)$ gases. The Ir(10%)SeU /C samples were prepared with different selenourea contents, with metal (Ir) to SeUmolar ratios of 1:0.1, 1:0.13, 1:0.25 and 1:0.5; and were denoted as IrSeU/C-**1**, IrSeU/C-**2**, IrSeU/C-**3** and IrSeU/C-**4**, respectively. Catalysts for gas diffusion electrode (GDE) experiments had utilized 20% iridium loading to improve charge distribution and reduce inner resistance of the catalytic layer. Here, only the most active system, with Ir to *SeU* molar ratio of 1:0.1, was taken into consideration. To make

comparison to *SeU*-free nanoparticles, the following catalysts Ir (10%)/C and Ir(20%)/C were synthesized under analogous conditions.

The electrochemical measurements were performed with CH Instruments (Austin, TX, USA) Model 750D and 920D workstations. A mercury-mercury sulfate electrode (Hg/Hg_2SO_4) was used as a reference electrode; and all potentials were expressed against the reversible hydrogen electrode (RHE). Glassy carbon rod or platinum sheet served as counter electrode. Rotating ring disk electrode (RRDE) experiments were performed using a variable speed rotator (Pine Instruments, USA). The electrode assembly utilized a glassy carbon disk (with geometric area of $0.247\,cm^2$) and a Pt ring. The collection efficiency (N) of the RRDE assembly, as determined from the ratio of ring and disk currents (at 1600 rpm) using the argon-saturated $0.005\,mol\,dm^{-3}\,K_3[Fe(CN)_6]$ in 0.1 mol $dm^{-3}\,K_2SO_4$ solution, was equal to 0.388. For glassy carbon electrodes covered by electrocatalytic films of Pt/C, Ir/C, IrSeU/C-**1**, IrSeU/C-**2**, IrSeU/C-**3** and IrSeU/C-**4** the N values were as follows: 0.375, 0.374, 0.383, 0.376, 0.393 and 0.382, respectively. In other words, the N values are comparable and imply analogous morphologies of our thin-film catalytic systems. This view is consistent with scanning electron microscopic (SEM) examination of the catalytic surfaces (for simplicity not shown here). The values of N (estimated separately for each layer) have been further used to calculate the relative (%) amount of H_2O_2 produced during oxygen reduction.

Before experiments, working electrodes were polished with aqueous alumina slurries (grain size, $5-0.05\,\mu m$) on a Buehler polishing cloth. In the course of RRDE experiments, in order to oxidize H_2O_2 (generated at the disk) under the convective-diffusional mass transport control, the potential of the ring electrode was kept at 1.23 V vs. RHE. The activity of examined catalysts was also tested with a home-made gas diffusion electrode (GDE, geometric area of active part, $0.916\,cm^2$) mounted into a Teflon holder with provision for gas feeding from the back of the electrode. A Pt ring served as a current collector. The gas diffusion backing layer for electrocatalysts was a carbon cloth (Designation B, 30% Wet Proofing; BASF Fuel Cell Co).

Catalyst layers were deposited on glassy carbon disk or carbon cloth by introducing (by dropping) appropriate volumes of inks containing catalytic nanoparticles and using 2–propanol and Nafion® (20% by weight) as solvent and binder, respectively. The glassy carbon electrodes covered with the catalytic layers were dried at room temperature, $22 \pm 2\,°C$. For GDE experiments, carbon clothes with deposited catalytic films were dried at $100\,°C$ to a constant weight followed by pressing them upon application of $2\,kg\,cm^{-2}$ for 30 s. The iridium loadings were $40\,\mu g\,cm^{-2}$ and $\sim 0.5\,mg\,cm^{-2}$ in cases of RRDE and GDE experiments, respectively. Working electrodes were rinsed with water in order to clean the surfaces from impurities followed by cycling in the nitrogen-saturated electrolytes in the potential range from 0.08 V to 0.92 V to activate the layers and reach stable responses.

Transmission electron microscopy (TEM) experiments were carried out with Libra 120 EFTEM (Carl Zeiss) operating at 120 kV. Scanning electron microscopic (SEM) measurements and energy-dispersive X-ray analysis were achieved using MERLIN FE-SEM (Carl Zeiss) equipped with EDX analyzer (Bruker). X-ray photoelectron spectroscopy (XPS) measurements were accomplished with Microlab 350 spectrometer having the maximum energy resolution 0.83 eV while using Al Kα nonmonochromatic radiation (1486.6 eV, 300 W) as the exciting source. The pressure during analysis was 5.0×10^{-9} Pa. The measured binding energies were corrected by referring to the energy of C 1s at 284.2 eV as the internal standard. XPS spectra were fitted with the use of Avantage 4.88 XPS software.