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Effect of heterogeneous oxidation on electrochemical properties of tailored $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$ sensing electrode of potentiometric DO sensor

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ABSTRACT

Effect of heterogeneous oxidation of the thick-film $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$ sensing electrode (SE) of the planar potentiometric dissolved oxygen (DO) sensor on its electrochemical properties has been investigated by field emission beam scanning electron microscopy (FIB-SEM), X-ray photoelectron spectroscopy (XPS), cyclic voltametry (CV) and electrochemical impedance spectroscopy (EIS) techniques. It was found that the most of heterogeneous oxidation has occurred during the first week of SE exposure to the aqueous environment leading to the partial oxidation Ru^{IV} to Ru^{III} occurred mostly on the grain boundaries of SE. The presence of the "inner" active surfaces in the bulk of the developed complex oxide SE has been reaffirmed. It was also found that heterogeneous oxidation caused the increase of the Cu 2p peaks intensity on the surface of SE after the water treatment for one month, which has been confirmed by XPS measurement.

1. Introduction

On-going in-situ monitoring of such water quality parameters as pH and DO at the different depths on the high spatial resolution has been highly demanded for environmental measurement and control. For this purpose reliable, simple, robust and inexpensive ceramic chemical sensors based on nano-structured semiconductor oxide SE being under extensive research during the last decade [1–5]. Recently, tailoring of nanostructured RuO_2 to the specific requirements of the water quality control on high spatial resolution has been resulted in the development of sub-micron Cu_2O- and ZnO-doped RuO_2-SEs for solid-state pH and DO sensors [6–10]. Specifically, miniature ceramic potentiometric sensor attached with screen-printed thick-film $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE has been exhibited the highest DO sensitivity, fast response/recovery time (few seconds) and very low interference to such dissolved ions as Cl^-, Li^+, SO_4^{2-}, NO^{3-}, Ca^{2+}, PO_4^{3-}, Mg^{2+}, Na^+ and K^+ in the solution in a concentration range of 10^{-7} to 10^{-1} mol/L [11]. Since antifouling properties of Cu_2O and ZnO are well-known [12], the developed $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE has also shown high resistance to bio-fouling in the lake [6] and sewerage environment [7], and consequently, 20 mol% Cu_2O-doped RuO_2-SE has been considered as one of the promising candidates to the practical SE of the water quality sensors [11]. However, it has also been reported that some of the sensor's characteristics were drifted during the first month of sensor's operation due to the heterogeneous oxidation of SE [2,13]. Therefore, from the chemical sensors development point of view, investigation of the effect of heterogeneous oxidation of the thick-film $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE on its electrochemical properties is vital. Consequently, this research represents the study towards the better understanding of the influence of heterogeneous oxidation of the newly-developed complex oxide $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE on its electrochemical properties.

2. Experimental

$Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SEs were fabricated from Cu_2O and RuO_2 nano-particles of high-purity analytical grade which had a particle size range of ca. 46 and 360 nm, respectively [11]. In brief, Pt current conductors of ca. 5 μm thickness were applied onto each alumina sensor substrate and sintered at 1000 °C for 1 h in air prior to RuO_2 and Cu_2O nano-particles deposition. This was followed by the screen-printing of thick-film SEs, which were obtained by mixing Cu_2O and RuO_2 nano-powders with organic α-terpineol ($C_{10}H_{18}O$, 99.9%) suspension as a binder. The subsequent sintering of SEs at 800 °C in air was followed. All fabricated ceramic sensors attached with the developed complex oxide $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SEs were covered by the glazing layer except the active surfaces of SEs and were subsequently annealed at 600 °C for 30 min.

The surface morphology of the $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SEs was investigated by using a HELIOS-Nanolab-600 (The Netherland) FIB-SEM with Ga beam capable to cut the developed $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE through in order to observed and analyse the SE/substrate interfaces. The thickness was determined in each case by observing the cross section of the $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SEs. XPS measurements (XPS; AXIS-165, Shimidzu/Kratos, Japan) were performed using a monochromatic aluminium X-ray source (1386.6 eV) operating at 15 kV and 7 mA under ultra-high vacuum (10^{-5} Pa). The adventitious carbon peak at 284.6 eV

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was used as a reference to estimate the electrical charge effect. CVs were performed from −1.0 to 1.0 V at a scan rate of 100 mV s^{-1} in a KH_2PO_4–Na_2HPO_4 solution to observe the changes of the electrochemical characteristics of the developed $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE during heterogeneous oxidation within the first month of usage. EIS analysis of $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE was performed using AUTOLAB analyser, PGSTAT, The Netherlands. Impedance spectra were collected in the frequency range of 1 Hz to 1 MHz at amplitude 5 mV at different pHs. A separated external Ag/AgCl, Cl^- reference electrode was used for potentiometric measurements.

3. Results and discussion

Fig. 1(A) shows SEM image of $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE deposited on the alumina sensor substrate. This SEM image exhibited that the developed $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$ structure consists of the grains, which were homogeneously distributed in the relatively dense SE. Pores sized from ~600 to ~900 nm were also developed. The insert depicts a water droplet on the surface of the developed $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$ with water contact angle of 130° confirming the super-hydrophobic nature of $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE and the presence of a large number on the hydroxyl groups on its surface [14]. Therefore the main feature

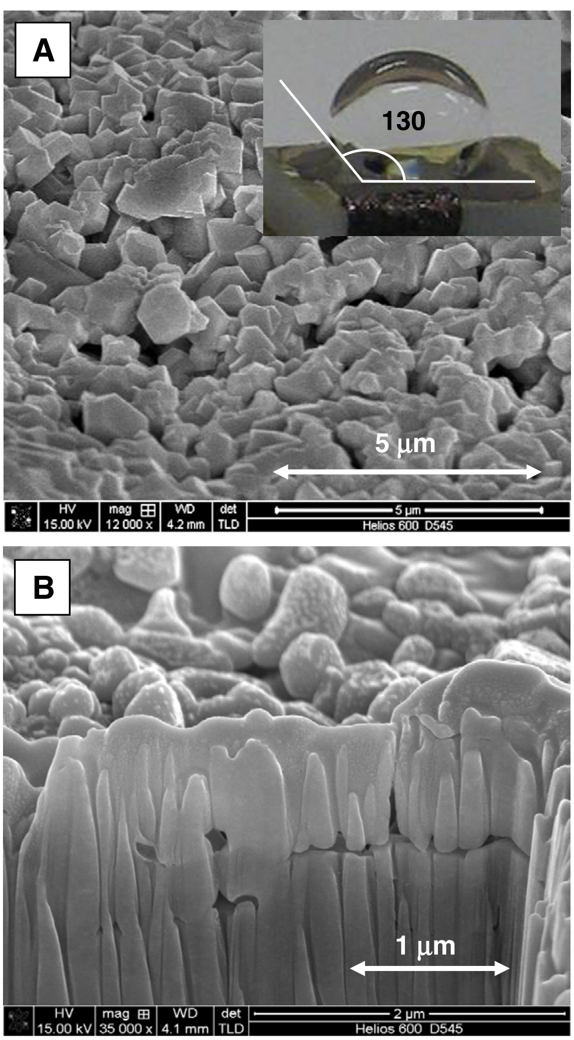

Fig. 1. SEM images of 20 mol% Cu_2O-doped RuO_2-SE (A) with insert of a water droplet sits on the nanostructured SE indicating superhydrophobic property of its surface. SEM image of the FIB cut in thick-film $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE (B) confirming the development of active "inner" surfaces.

distinguishes the complex oxide SEs which is their surface structure in a solution. Fig. 1(B) encapsulates how the FIB cuts were made in the thick-film $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE. Measurements of the several grain sizes of film-SEs were made by using FIB cut in the structure of SE. Analysis of these measurements revealed that the thickness of the thick-film-SE was about 3.0–5.0 μm with the average grain size of about 1.0–2.0 μm. Unfortunately Ga beam made interface smoother during the cut. As a result, the roughness of the developed interfaces cannot be observed. FIB cuts in the structure of the thick-film SEs have also confirmed the presence of the "inner" active surfaces of SE [15] sized form 50 to 110 nm.

The as-prepared samples of SE were measured by XPS analysis to investigate the changes in surface hydroxyls with time (Fig. 2). After that they were subjected to the water treatment for one month with subsequent XPS analysis. All spectra presented in Fig. 2 were re-calibrated for adventitious carbon peak at 284.6 eV. The Ru 3d core level spectrum was characterised by the pair of narrow peaks corresponding to the 5/2 and 3/2 spin-orbit components at 285.0 and 281.0 eV, respectively. After one month exposure to water, the peak representing Ru 3d core level changed considerably, suggesting modifications in the electronic structure of the doped RuO_2-SE. The survey XPS specrum of the Cu 2p spectral region for Cu_2O revealed the presence of only two distinguished peaks without any obvious contaminant species. Interestingly that after the water treatment for one month the intensity of Cu 2p peaks has been increased. One possible explanation of this effect is that Cu 2p concentration on the surface of SE has been increased due to the partial oxidation of Ru(IV) to Ru(III) within the SE structure discussed elsewhere [13]. Considering the changes that the Ru/RuO_2 sustained within the Cu_2O-doped SE, it may be reasonable to suggest that the reaction involved the transfer of two electrons in the following way [11]:

$$2RuO_2 + 2H^+_{ag} + 2e^- \leftrightarrow Ru_2O_3 + H_2O. \tag{1}$$

The O 1s region, as shown in Fig. 2(C), is characterised by two asymmetric profiles, indicating that at least two oxygen species are present on the surface. The first band at 529.8 eV attributed to lattice oxygen and the other at about 530.7 eV caused by surface hydroxyls [16]. It is clear that the amount of surface hydroxyls decreased with increasing time of water treatment, which is accompanied by the changes in wettability of the samples. Consequently, it can be concluded that under certain surface roughness the more the surface hydroxyls the more hydrophobic the SE surface.

CVs for $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE were in-situ recorded at different time intervals in KH_2PO_4–Na_2HPO_4 buffer solution at a temperature of 25 °C. They are shown in Fig. 3. The presence of heterogeneous oxidation has been clearly visible in the behaviour of the curves. For the freshly prepared $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE two cathodic and two anodic peaks were observed within the measuring potentials range. On the positive potential range only surface reactions associated with the redox pairs $Ru^{III} \leftrightarrow Ru^{IV}$ and corresponding H^+ adsorption occur [3]. However, after just one week two anodic peaks disappeared and the intensity of the measured current decreased. CV for $Cu_{0.4}Ru_{3.4}O_7 + RuO_2$-SE recorded after one month has shown not much difference from the CV recorded after the first week, suggesting that the most of the heterogenic oxidation has occurred during the first week. During potential sweep, the oxide surface is oxidised and reduced, reversibly exchanging protons with the solution, as described elsewhere [15]:

$$RuO_x(OH)_y + \delta H^+ + \delta e^- \leftrightarrow RuO_{x-\delta}(OH)_{y+\delta} 0<\delta<2. \tag{2}$$

CV curves can also provide ΔE_p values, i.e. the potential difference between couples of anodic and cathodic peaks. A high value of ΔE_p normally indicates irreversibility for reactions of dissolved species in case of the redox reactions on active oxide surface sites of