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Effect of ZnO doping on morphology and electrochemical properties of sub-micron RuO_2 sensing electrode of DO sensor

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ABSTRACT

Thick-film 20 mol% ZnO-doped RuO_2 sensing electrodes (SEs) were fabricated by screen-printing technique on the platinised alumina substrate of the planar electrochemical dissolved oxygen (DO) sensor. The effect of ZnO doping on morphology, electrochemical properties and sensing characteristics of the sensor was investigated. It was found that ZnO doping has not only improved the SE structure, but has also enhanced selectivity of the DO sensor. Selectivity testing exhibited that the presence of Cl^-, Li^+, SO_4^{2-}, NO^{3-}, Ca^{2+}, PO_4^{3-}, Mg^{2+}, Na^+ and K^+ with a concentration range of 10^{-7} to 10^{-1} mol/L in the solution had practically no effect on the sensor's *emf*. The reason in enhancement of the sensor characteristics could be related to the establishment of the better structured SE as more advanced crystallization is achieved for the doped RuO_2-SE.

1. Introduction

Nanostructured RuO_2 is an electronically conductive semiconductor oxide with rutile structure. Due to its high catalytic activity it has been considered as one of the promising materials for a variety of applications such as super-capacitors, bio-sensors and potentiometric pH and DO sensors [1,2]. Doping of RuO_2 by other nanostructured noble metals or nano-oxides has often being very effective method of improvement not only the structure of RuO_2-SE, but also its electrochemical properties [3–5]. Moreover, high surface-to-volume ratio of nano-particles and their associated high surface activities can vary the kinetics of redox reactions in water for the doped-SEs. Therefore, from the embedded chemical sensor's development point of view, doped thin- and thick-film RuO_2-SEs possess the electrode structure with increased adsorption capability toward DO (pH) sensing. However, some noble metals, such as Pt, Au and Rh, are too expensive to be used on an industrial scale. Consequently, research of nano-oxide-doped RuO_2-SE has a significant practical value. Our previous attempts in the development of Cu_2O-doped RuO_2-SE have shown that it is possible to improve both the sensor's selectivity and its antifouling resistance [6,7]. Since ZnO is also a well-known oxide with reported antifouling capabilities [8], it is essential to investigate its influence on the morphology and electrochemical properties of RuO_2-SE. To the best of our knowledge, no study has been dedicated so far to the analysis of such influence relevant to the electrochemical water quality sensors.

Thus, this research represents the first study towards the better understanding of the influence of ZnO doping on the morphology and electrochemical properties of sub-micron RuO_2-SE of the potentiometric DO sensor.

2. Experimental

20 mol% ZnO-doped RuO_2-SEs were fabricated from the ZnO and RuO_2 nano-particles of high-purity analytical grade which had a particle size range of *ca.* 50 and 360 nm, respectively. 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 ZnO nano-particles deposition. This was followed by the screen-printing of thick-film SEs, which were obtained by mixing ZnO and RuO_2 nano-powders with organic α-terpineol ($C_{10}H_{18}O$, 99.9%) suspension as binder [6]. All fabricated sensors attached with 20 mol% ZnO-doped RuO_2-SEs were subsequently sintered at 800 °C.

The surface morphology of the ZnO-doped RuO_2-SE was characterized by a JEOL JSM-6340F field emission scanning electron microscope (FE-SEM). X-ray photoelectron spectroscopy (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 carbon peak at 284.6 eV was used as a reference to estimate the electrical charge effect. X-ray diffraction (XRD) analyses were carried out using a Bruker D8 Advance X-Ray Diffractometer with CuKα (with wavelengths $K\alpha_1\lambda = 1.5406$ Å, $K\alpha_2\lambda = 1.544439$ Å and a $K\alpha_2$ ratio of 0.5) radiation operating at 40 kV, 40 mA and monochromatised with a graphite monochromator. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV s^{-1} in a KH_2PO_4–Na_2HPO_4 solution to observe

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the electrochemical characteristics of ZnO-doped RuO_2-SE. The electrochemical measurements of complex impedance were 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. Dissolved salt solutions including KCl, KBr, Li_2SO_4, Na_2SO_4, $Mg(NO_3)_2$, $Ca(NO_3)_2$ and Na_2HPO_4 were used to determine the electrochemical characteristics of the SEs including their cross-sensitivity, selectivity limits of detection and working concentration span. Concentrations of 10^{-7} to 10^{-2} mol/L in aqueous solutions of these salts were prepared from 10^{-1} mol/L stock solutions. A separated external Ag/AgCl, Cl^- reference electrode was used for potentiometric measurements.

3. Results and discussion

Fig. 1 depicts both SEM images of ZnO-doped RuO_2-SE and XRD patterns of this SE deposited on the alumina sensor substrate. As shown in Fig. 1(A), the structure of ZnO-doped RuO_2-SE consists of the grains, which were homogeneously distributed in the relatively dense SE. Few pores were also developed. It can be observed that the particles appear to be made up of a combination of tetragonal, cubic and rhombohedral structures sized between 500 and 900 nm, as presented in Fig. 1(B). The XRD spectra of the ZnO-doped RuO_2-SE presented in Fig. 1(C) showing the RuO_2 diffraction pattern is consistent with a tetragonal structure with a symmetry or space group *P42* and lattice parameters $4.499 \times 4.499 \times 3.107$ Å <$90 \times 90 \times 90$>. The hexagonal, P63 phase of ZnO was similarly identified with lattice parameters $3.25 \times 3.25 \times 5.207$ Å <$90 \times 90 \times 120$>. In both cases, identification was assisted by the high narrow diffraction peaks, suggesting a high degree of crystallinity of the developed structure. A number of rhombohedral alumina peaks with lattice parameters $4.759 \times 4.759 \times 12.993$ Å <$90 \times 90 \times 120$> are also noted, however, their intensity was somewhat low.

XPS analysis of 20 mol% ZnO-doped RuO_2-SE is presented in Fig. 2, with (A) showing the characteristic binding energy shape of the core level spectra for Zn $2p_{3/2}$, (B) the characteristic binding energy shape of the Ru 3d shell electrons and (C) spectrum of the O 1s spectral region. Due to the fact that the XPS data for Ru 3d encompassed the C 1s peak for adventitious carbon at 284.6 eV, all spectra illustrated in Fig. 2, have been recalibrated by the carbon peak. The survey XPS spectrum of the Zn $2p_{3/2}$ spectral region for ZnO revealed the presence of only zinc and oxide without any obvious contaminant species. In the Zn 2p core level XPS spectrum, the peak corresponding to the Zn $2p_{3/2}$, is observed at around 1015 eV. The Ru 3d core level spectrum

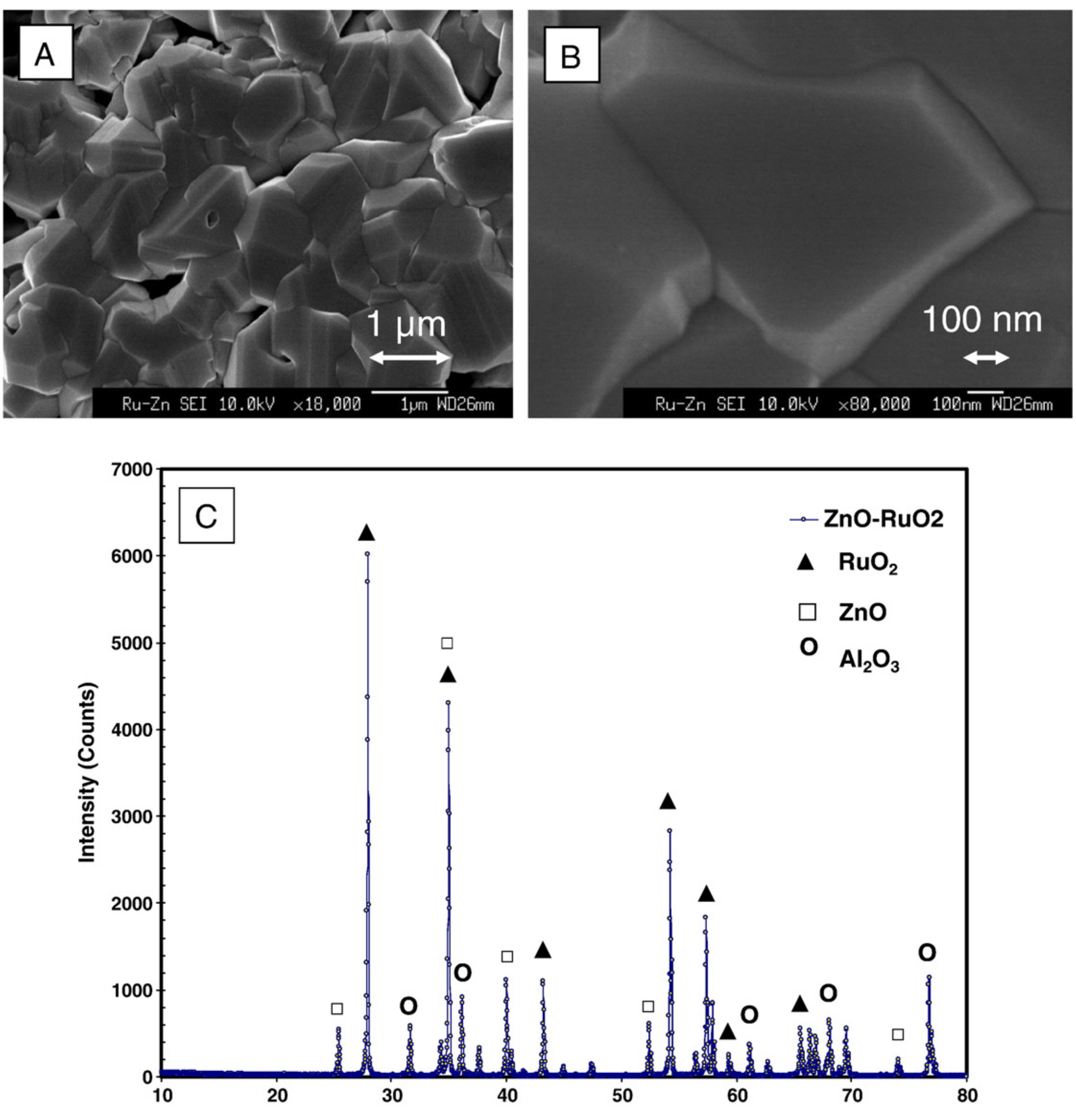

Fig. 1. SEM images of 20 mol% ZnO-doped RuO_2-SE illustrating surface morphology (A), magnified view of the main grains at nano-scale (B) and XRD patterns of SE deposited on Al_2O_3 sensor substrate (C).