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Influence of Sintering Temperatures on the Performance of ZnO-doped RuO_2 Sensing Electrode of Electrochemical DO Sensor

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Abstract:
In this research planar dissolved oxygen (DO) sensors based on 20 mol % ZnO-doped RuO_2 thick-films were fabricated on alumina substrates over a range of sintering temperatures (STs) during the preparation. The STs were 750, 800, 850, and 900^{o}C. Subsequent scanning electron microscope (SEM) images showed that different surface morphologies were achieved for the different STs. The relationship between DO and the sensor's response at STs of 800 and 850^{O}C was found to be relatively linear for all four STs. It has been experimentally established that optimum results were obtained when the sensing (SE) was sintered at 800^{O}C. The correlation between pH and SE response was found to be linear and showed there was minimal impact of the ST on the SEs.

Key words: RuO_2, Sensing Electrode, Electrochemical Sensor, Dissolved Oxygen

Introduction

Currently, the availability of a reliable water supply along with satisfactory water quality is an important issue. Therefore, if accurate measurement of DO concentration is required on high spatial resolution, cheap, robust, miniature electrochemical sensors would likely be the most preferable option [1,2]. One aspect of this discussion is the need to adequately monitor water quality in real time to allow decision support for water management. In this context solid-state water quality sensors based on nano-structured film-SEs show significant potential for this application. The further development of these devices, presented in this paper, is based on trying to achieve improvements by investigation of the relationship between the SE ST and the DO and pH sensing capability. Previous studies indicated that doping of nano-structured semiconductor SEs with relatively low concentrations of nano-oxides was an effective method for improving both physical properties and chemical response of the SE [3-6]. In the current research more emphasis is placed on understanding the water DO measurement performance of the nano-structured SE, when the SE is sintered at different temperatures of 750, 800, 850 and 900^{o}C. The sensing characteristics of the developed electrochemical DO sensors were investigated at the different temperatures in the water solutions, where DO and pH was controlled.

Results and Discussion

The morphology and structure characterization of the SE sintered at the different temperatures were studied by examining the SEM images of the SE presented in Fig. 1. These images show significant differences in the physical structure of SEs when they were prepared at different STs. At a ST of 750^{o}C (Fig. 1A), it is clear that the nano-particles are homogeneously distributed across the film with relatively low number of adsorption centers on the surface of SE. These observations suggest that not all of the sintering reactions required for optimal SE sensitivity occurred, therefore giving rise to an incomplete ZnO-RuO_2-SE structural configuration. In contrasting, the images presented in Figs. 1B and 1C demonstrate a significant improvement in the formation and morphology of SE. At these temperatures , the nano-particles are made up of hexagonal, tetragonal and cubic structures and are not only homogeneously distributed in the dense SE structure; but also have a higher number of adsorption centers as shown by the many grain boundaries, which is important in the consideration of reactions occurring on the particles' surface. Furthermore, the highly granular surface configuration of the sensor strongly indicates that the structure has a relatively high surface area-to-volume ratio

which ultimately increases the sensitivity of the sensor. The images also suggest that the structures are not porous, and hence have not undergone a melting process. On the other hand, a ST of 900°C results in a SE with an open pore structure, and comparably low number of adsorption centers. Additionally, this material has a low surface-to-volume ratio, which is likely to decrease the SEs DO sensitivity. This indicates that the reactions that occurred at 900°C exceeded the desired pattern and other superfluous surface reactions may have occurred. These findings signify that the sensor's optimum ST lies between 800 or 850°C.

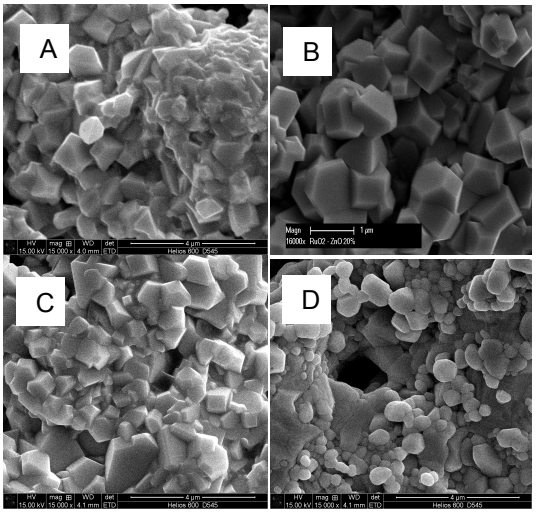

Fig. 1. SEM images of the 20 mol % ZnO-doped RuO_2-SE sintered at different temperatures: (A) 750°C; (B) 800°C; (C) 850°C and (D) 900°C.

Fig. 2 shows cyclic voltammograms (CV) recorded in-situ on different 20 mol % ZnO-doped RuO_2-SEs sintered at STs of 750°C, 800°C, 850°C and 900°C, respectively. CVs were recorded at a temperature of 16.8°C using $K_3Fe(CN)_6$ – 0.1M KCl buffer solution (pH 7.26). For all 20 mol % ZnO-doped RuO_2-SEs sintered at STs two cathodic and two anodic peaks of different intensity were observed within the measuring potential range. The shape of CVs was similar to the CVs recorded for 20 mol % Cu_2O-doped RuO_2-SE sintered at 800°C [7]. These measurements were used in the attempt to understand the electron transfer across the surface of the complex oxide-SE and acquiring information about material diffusion limit process and electron adsorption rate. The recorded CVs are also shown that the ST does have an effect on the electrochemical characteristics of the developed SEs.

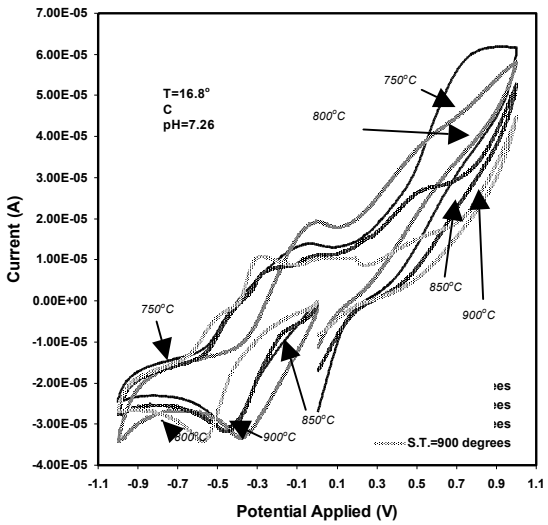

Fig. 2. CVs at scan of 100 mV/s for 20 mol % Cu_2O-doped RuO_2-SEs sintered at different temperatures in $K_3Fe(CN)_6$–0.1M KCl buffer solution at a temperature of 16.8°C.

The FTIR spectra for 20 mol % ZnO-doped RuO_2-SEs yielded extremely interesting results in perturbation region of the spectrum. It produced several uncompensated water vapor bands with various intensities in the region of 3000-3600 cm^{-1}, as well as the peak observed at 1515 cm^{-1}. Although the intensities of the spectra are different in terms of absorbance values, general trends and observed peaks are very similar for all four (4) sintering temperatures. Two relatively large peaks observed at 3646 and 2750 cm^{-1} bands for all four spectra, confirm strong existence of O-H bonds. Comparatively large spike at 1740 cm^{-1} band indicates the presence of carbon dioxide (CO_2 bonding) and is present in all STs. The distinct stretch at 1260 cm^{-1} corresponds to O-H bonding, in this case the presence of alcohol ($(R)_3C$-OH functional group), most like ethanol which is still present, even after evaporation. The great area of importance is the perturbation section of the spectrum, where superoxide oxygen ions (O_2^-) adsorption peaks are observed at 400-810 cm^{-1}. The FTIR spectrum also suggests that there are no impurities present, since no other peaks were observed.

Fig. 3 shows potentiometric DO measurements for ZnO-RuO_2-SEs sintered at different temperatures. The assessment of the performance of SEs indicated that their DO sensitivity is proportional to the temperature at which the SE was sintered. By analyzing these graphs it can be concluded that the best linearity was obtained at ST of 800°C, with

sensitivity, shown by the Nernstian slope, of 44.5 mV/decade. Furthermore, although a more sensitive Nernstian slope of 50.4 mV/decade was achieved when the ST was 750°C, the linearity was relatively poor. Lastly, the worst possible result was obtained then ST was 900°C, where both linearity and Nernstian slope (21.6 mV/decade) was greatly diminished.

Conclusions

The main focus of this investigation was to study the effect of varying STs in the preparation of ZnO-RuO_2-SEs. The selected STs for these studies were 750°C, 800°C, 850°C and 900°C, respectively. In this investigation SEs sintered at various temperatures were successfully developed and tested for DO measurements to establish the optimum ST at which SE demonstrates the best sensing aspects. This research has established that although SEs have displayed an excellent adhesion to the alumina sensor substrate when all four (4) STs were applied, the fabrication conditions do have an overall effect on sensors' structural and electrochemical characteristics. The SEM graphs clearly demonstrate the vast difference in the complex structure of both SEs at various STs and hence it can be concluded that the best configuration was chemically achieved when the ST was either 800 or 850°C. These finding are also clearly verified when looking at the CV scans, which distinctively identify the contrast and variation in the ST of both sensors. Additionally, the obtained DO measurements for both SEs further support the fact that 800°C is perhaps the best possible ST, since at this sensors' preparation condition the optimum linearity and Nernstian slope was achieved. Lastly, it can be suggested and consequently concluded that the optimum ST is 800°C and therefore all future work regarding the sensor preparation must be completed by employing this ST.

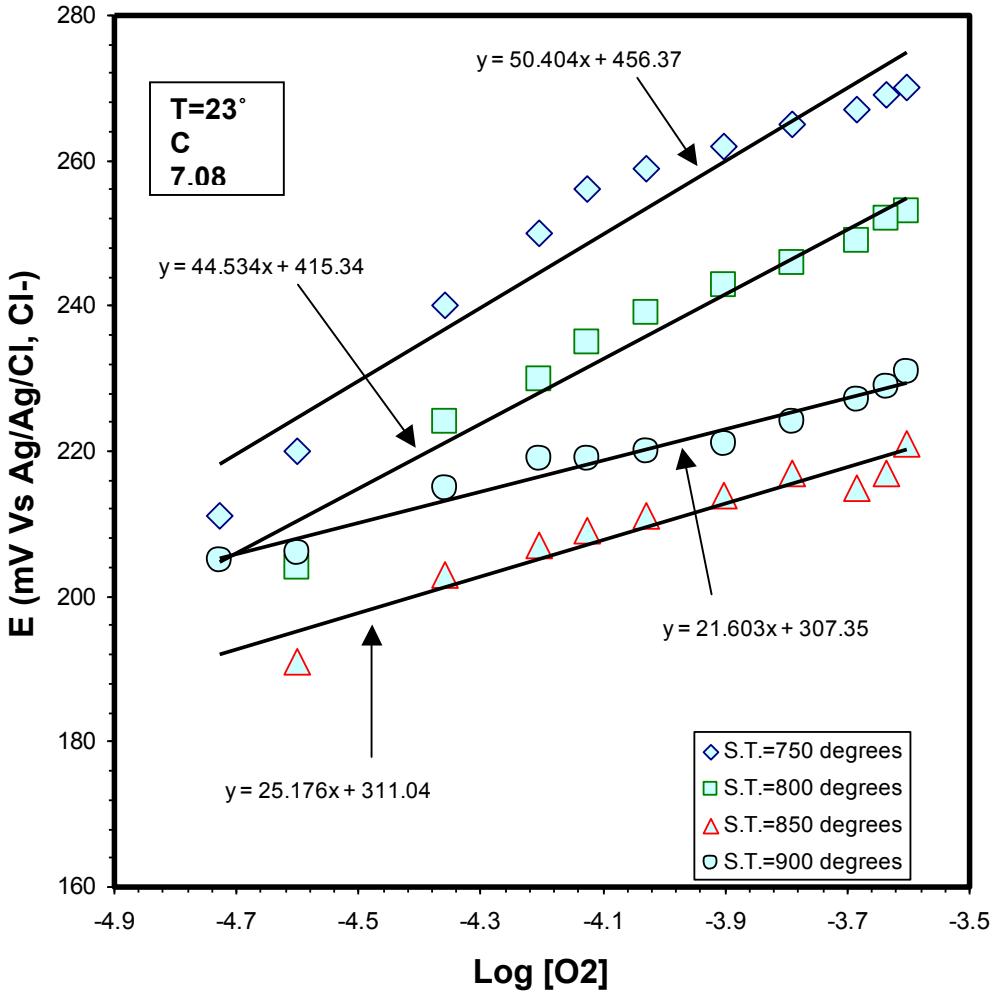

Fig. 3. Potential difference variations vs DO measured in water for 20 mol % ZnO-doped RuO_2-SEs at 23˚C (Various STs).

Acknowledgements

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