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Study of Pb(II) Effect on Electrosynthesis of Lead Dioxide in More Environmentally Electrolyte of Methanesulfonic Acid

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Lead dioxide has received much attention as an electrode material for its high resistance to corrosion, high electronic conductivity, good stability, long lifetime, and low cost. However, problems still exist concerning the selection of the electrolyte during electrodeposition, which may cause issues in energy conservation and environmental protection. The present study utilized the environmentally friendly electrolyte methanesulonic acid (MSA) and evaluated the effect of the Pb(II) concentration on the electrodeposition of lead dioxide in MSA using rotating disk electrode (RDE) voltammetry to determine the most suitable composition of the electrodeposition bath and to realize an environmentally and energy friendly process. We adequately characterised PbO_2 synthesized on a Pt electrode surface, and the results showed that the Pb(II) concentration had a great influence on the electrodeposition of lead dioxide in MSA. By controlling the composition of the electrodeposition bath to 0.2 M Pb(II) and 0.1 M MSA, we obtained an optimal reversible process, longer electrode lifetime and more satisfactory environmental protection.

Keywords: lead dioxide; Pb(II) concentration; environmentally electrolyte; RDE

1. INTRODUCTION

Zinc is mainly extracted from its sulfide ores, oxide ores or other secondary resources by means of an electrowinning process in hydrometallurgy. Lead dioxide (PbO_2), as the electrodeposit, is extremely attractive due to its good resistance to corrosion, high electronic conductivity, good stability in acidic media, long lifetime, low cost, and high overpotential for oxygen evolution compared with other materials [1-10]. During the electrowinning process, prominent problems arise, due to the selected electrolyte, which may cause in energy conservation and environmental protection. Traditional conditions proceed by using different concentration of Pb(II) in alkali or acid solution [11-13], Additionally, waste from the process may damage the environment to various extents. Selecting an appropriate electrolyte and suitable composition of the electrodeposition bath cannot be ignored.

Methanesulfonic acid (MSA), as an environmentally friendly electrolyte, has been used in the metal finishing industry due to its chemical stability, high ion conductivity, biodegradability and low toxicity [14-17]. However, most studies have focused on the application of MSA in, undivided, soluble lead-acid flow batteries, Studies of producing stable PbO_2 electrodeposits by controlling the concentration of Pb(II) in MSA solutions during the electrowinning process in hydrometallurgy are scarce [18-20]. Alexandre Oury and co-workers have focused on studies of the electrodeposition cycling of lead dioxide (PbO_2) on vitreous carbon electrodes in lead methanesulfonate for applications in soluble lead acid flow battery application [21-22]. Velichenko, who focused on the nucleation and growth mechanism of PbO_2, concluded that the current efficiency increases at a higher temperature and Pb(II) concentration and at a lower MSA concentration[23-24]. Compared to classical acidic media, the presence of methanesulfonate ions yields a higher deposition rate resulting in thicker coatings without changing the mechanistic aspects [20,22]. As an important part of the composition, it is then important to investigate the effect of the Pb(II) concentration on the electrodeposition of lead dioxide in MSA and adequately characterise the PbO_2 synthesized on a Pt electrode surface to ensure the most suitable concentration of Pb(II) is utilized in the electrowinning process.

The aim of this work is to study and carry out the effect of the Pb(II) concentration on electrodeposition of lead dioxide in more environmentally electrolyte of MSA. An alternative way to achieve this goal is to use the Koutechy-Levich equation to calculate the effect of the Pb(II) concentration on diffusion coefficient D and the apparent heterogeneous rate constant k of the electrodeposition process and to express the relative contributions of mass transport and kinetics. The phase compositions and surface microstructures of deposits synthesized on a platinum surface were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). Electrochemical characterisation by linear and cyclic voltammertry was also performed to study the reactions and the electrochemical stability. The results gained by changing the Pb(II) concentration in the study of the electrochemical behaviour were illustrated, specifically when using a rotating disc electrode (RDE), which is a well-established experimental technique to study the mechanism of electrochemical reactions and to determine their kinetic parameters [25-33].

2. EXPERIMENTATION

2.1. Apparent heterogeneous rate constant and diffusion coefficient.

According to the Koutecky-Levich equation, we can calculate the values of the apparent heterogeneous rate constants (k) and diffusion coefficients (D) for Pb(II) oxidation from a linear plots of I^{-1} versus $\omega^{-1/2}$:

$$I^{-1}=(0.62nFAD^{2/3}v^{-1/6}C\omega^{1/2})^{-1}+(nFAkC)^{-1} \qquad (1)$$

where n is the effective number of electrons exchanged in the reaction, F the Faraday constant (C/mol), A the surface area of Pt-RDE (m^2), v the kinematic viscosity of the solution (m^2/s), C the bulk concentration of the reacting species (mol/m^3) and ω the angular velocity of Pt-RDE (rad/s). Among which kinematic viscosity (v) is calculated by the equation:

$$v=\mu / \rho \qquad (2)$$

where μ is the dynamic viscosity of the solution (Pa·s), which was measured by a Brookfield viscometer, and ρ is the density of the solution (kg/m^3) that represents the ratio of mass and volume.

2.2. Physical and electrochemical characterization.

To investigate the chemical kinetics, the synthesized PbO_2 was examined by sensitive and widely used techniques for the chemical kinetics investigation of cyclic voltammetry and rotating disk electrode (RDE) voltammetry techniques. All the cyclic voltammetry experiments were obtained using aqueous solutions of Pb(II) and MSA at different ratios of room temperature. Galvanostatic deposition was carried out at a controlled Pb(II) concentration, in the range of 0.05 ~ 0.3 M. The MSA concentration was maintained at 0.1 M during all the experiments. The solution was equipped with the analytical grade reagents (AR) and twice-distilled water was used for all the solutions and high purity nitrogen gas was bubbled into the solutions for 20 minutes before applying the potential. A Pt RDE (Ametek) with an exposed Pt area of 0.196 cm^2 mounted onto a rotator, a platinum electrode and a Saturated mercurous sulfate electrode (SMSE) made up the “three-electrode system”, where the distance between the capillary and the working electrode surface was approximately 4d (d =diameter of the capillary). Cyclic voltammetry curves and anodic polarization curves were obtained using a P.A.R. potentiostat/galvanostat (model no. PARSTAT 2273) connected to a desk computer for data acquisition and control. All the potentials are given against SCE.

The phase composition and the surface microstructure characteristics of the synthesized PbO_2 on the Pt-RDE were also studied by means of X-ray diffractometer (XRD, D/Max-2200, model Empyrean) and scanning electron microscope (SEM, Nova NanoSEM450, model VEGA 3 SBH) to clarify the physical performances of these electrodes. The samples for the galvanostatic polarisation measurements (10 mA/cm^2) were prepared in different solutions with a synthesis time of 2 h, at a temperature of 20°C [29,34].

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry study

Fig. 1 shows the voltammograms measured in the solution of 0.2 M Pb(II) + 0.1 M MSA and a blank solution (0.1 M MSA). Two curves indicate the progressive increase of the current density with time, but the measured values are rather different depending on the electrolyte composition. The only one peak D in the blank curve is related to oxygen evolution. In contrast, there are three peaks in the red curve that are related to the presence of Pb(II) and are referenced with letters (A to C). Among these peaks, peak B on the anodic scan corresponds to the oxygen evolution, peak A corresponds to the oxidation process of Pb(II)→PbO_2, and peak C corresponds to the reduction process of PbO_2→Pb(II). The XRD data, shown in Fig 5, also support these assignments [35-37]. Furthermore, Fig. 1 demonstrates that the absolute current density values of the anodic peak ($0.0073 A\cdot cm^{-2}$) and the reduction peak ($-0.0074 A\cdot cm^{-2}$) are nearly the same, which indicates a reversible process [38]. In this way, by controlling the concentration of the electrodeposition bath, we can get the effect of extending the lifetime of the electrode and saving energy at the same time.

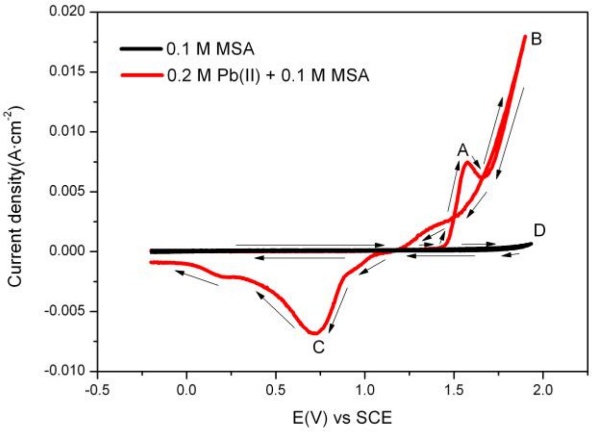

Figure 1. Cyclic voltammogram of a Pt electrode in 0.2 M Pb(II)+ 0.1 M MSA solution, in comparison with a blank solution (scan rate, 50 mV/s).

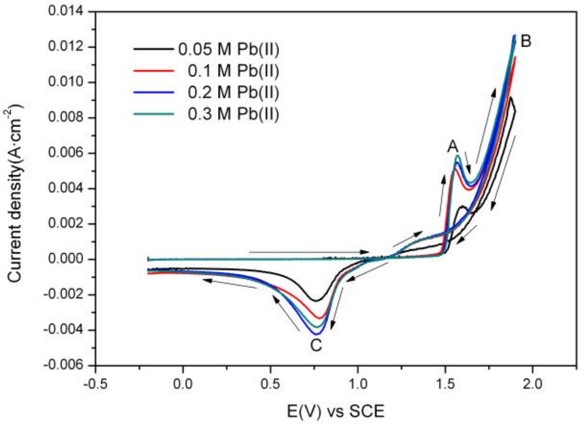

Figure 2. Cyclic voltammogram of a Pt electrode in solution of different Pb(II) concentrations, MSA controlled at 0.1 M (scan rate, 50 mV/s).

Fig. 2 shows the current density vs electric tension curves during PbO_2 electrodeposition with different concentrations of Pb(II) in the baths (MSA controlled at 0.1 M). The intensity of peak A proportionally increases as the Pb(II) concentration increases, which confirms that peak A results from

Pb(II) oxidation. On the cathodic scan of the curve, the intensity of peak C, which can also reflects the entire weight of the formed PbO_2 generated in the anodic scan [39], increases with an increase of the Pb(II) concentration as well. The absolute value of the intensity of peak C reaches a maximum near a value of -0.0074A·cm^{-2} with an oxidation current density of 0.0073A·cm^{-2}, when the Pb(II) reaches 0.2 M, indicating that the process at this composition is more suitable and can be regarded as a more reversible process.

3.2. Rotating disk electrode study

Fig. 3 illustrates the anodic polarization curves in 0.1 M MSA as a function of different concentrations of Pb(II) at a scan rate of 50 mV/s and rotating speeds varying from 100 to 800 rpm. The anodic polarization curves for each rotating speed were averaged over at least two experiments carried out under the same conditions, considering recorded eight cycles each time. The anodic polarization curves in MSA medium were found to show the same trend. The figure shows that the intensity is negligible at the beginning of the potential range from 0.5~1.5 V and becomes appreciable at approximately 1.6~1.8 V. The intensity increases with an increased rotating speeds and finally reaches a plateau as the rotation speed approaches 800 rpm, which proves that varying the rotation speeds can obviously affects the peak intensity within this stable region. The result is tangible proof that the mass transfer of Pb(II) to the electrode surface limits the rate of the electrochemical process.

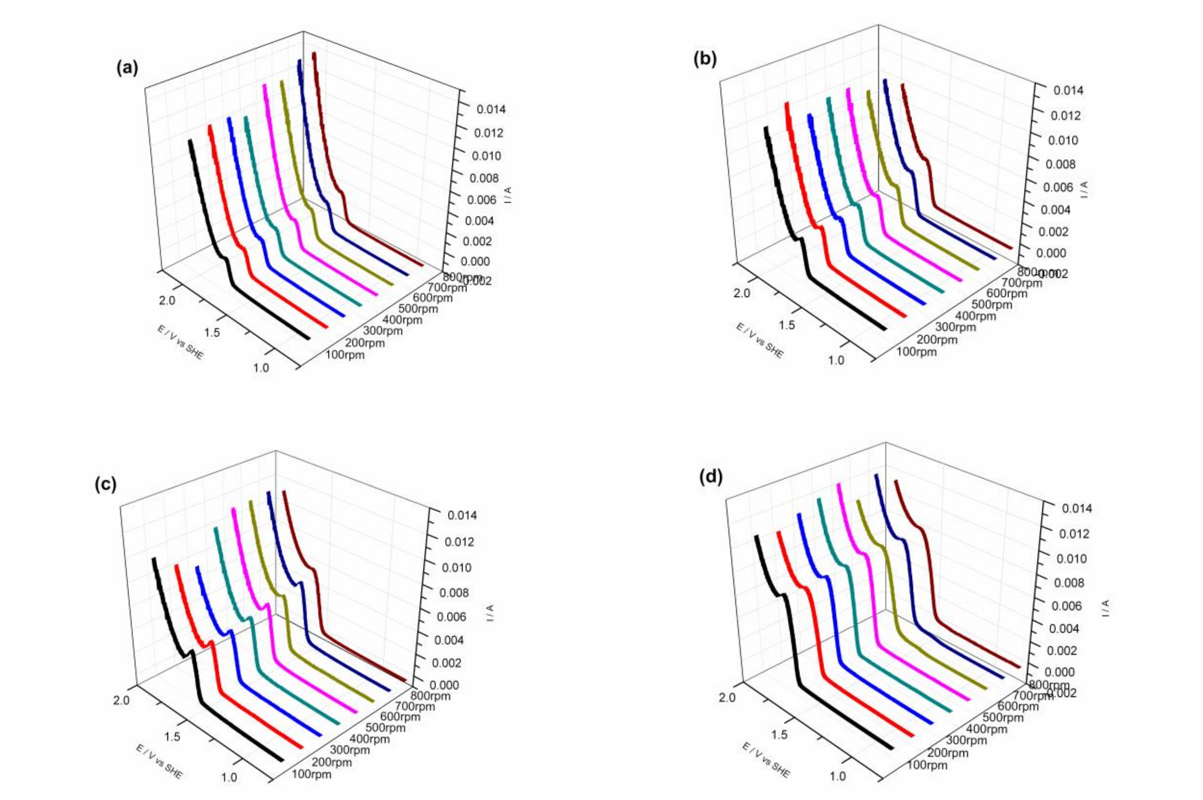

Figure 3. Anodic polarization curves of a Pt RDE in solutions of different Pb(II) and rotating speeds, (a): 0.05 M Pb(II), (b): 0.1 M Pb(II), (c): 0.2 M Pb(II), (d): 0.3M Pb(II), MSA controlled at 0.1 M (scan rate, 50 mV/s).

The Koutechy-Levich plot obtained at the diffusion plateau (1.66 V) with different Pb(II) concentrations are shown in Fig. 4, in which the curves not only indicate the direct proportionality of I^{-1} versus $\omega^{-1/2}$ but also show different intercepts on the I axes, proving that the reactions are under mixed control (ion transport and kinetics) at 1.66 V [40-41]. Some authors have proposed that the PbO_2 formation in acidic media is controlled by ion transport and kinetics. Pletcher and co-workers studied the behaviors of electrodeposits obtained in the presence of electrolyte and found that a mixed control was present [42-43]. Dai Qinzhou also confirmed that the process is influenced by ion transport and kinetics during the electrochemical oxidation process [44]. Curves fit to the obtained data points obtained and the goodness of each fit of each line are shown below. Fig. 4 also shows the diffusion coefficient D calculated from the value of the slope via Eq (1).

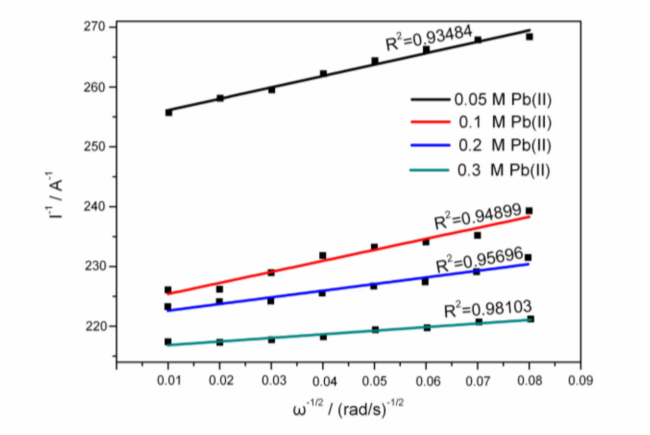

Figure 4. Koutechy-Levich plot obtained at diffusion plateau (1.66 V) of different Pb(II) concentrations.

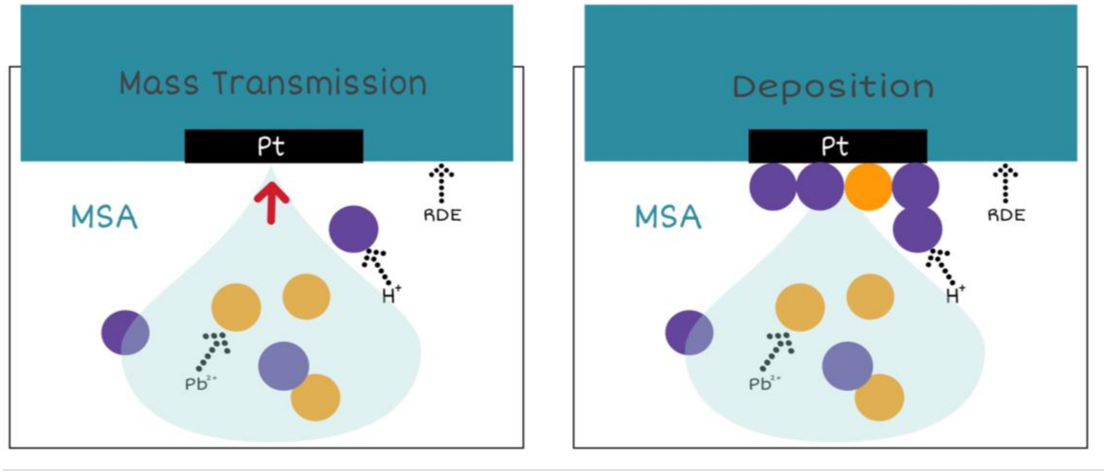

Figure 5. Process of PbO_2 electrodeposition on RDE surface in MSA

Table 1 shows the values of the parameters used in the equation and the results of all the calculations collected in this work. Importantly, the diffusion coefficient D and apparent heterogeneous rate constant *k* have an obvious relationship with the Pb(II) concentration of the solution. The value of the diffusion coefficient decreases with an increase of the Pb(II) concentration is observed, which is in accordance with some previous research [45-46]. All the conditions are based on assumption that the reaction at 1.66 V corresponds to Pb(II)→Pb(IV) [47] (hence n=2) and on the apparent heterogeneous rate constant *k* calculated from the value of the intercept of the fitted line. It can be noticed that the value of the rate constant *k* increases at first and then decreases as the Pb(II) concentration changes from 0.05 M to 0.3 M, which could be explained by the low Pb^{2+} concentration (<0.2 M), enhancing the formation of PbO_2 as shown in Formula 3. On the other hand, a higher Pb(II) concentration (>0.2 M) would also promote the reaction towards the opposite direction, causing excess Pb^{2+} to adsorb onto the surface of the electrode, which would affect the rate of the reaction. Fig. 5 shows the process of the PbO_2 electrodeposition.

$$PbO_2+4H^++2e \rightleftharpoons Pb^{2+}+2H_2O \qquad (3)$$

Table 1. Verification of Koutecky-Levich equation

Pb(II) Concentration	Koutecky-Levich equation: $I^{-1}=(0.62nFAD^{2/3}v^{-1/6}C\omega^{1/2})^{-1}+(nFAkC)^{-1}$							
	nF (C/mol)	*C* (mol/m^3)	*A* (m^2)	*v* (m^2/s)	Intercept	Slope	*k* (m/s)	*D* (m^2/s)
0.05 M	1.93×10^5	50	1.96×10^{-5}	2.27×10^{-6}	254.6	194.62	3.6×10^{-4}	6.83×10^{-10}
0.1 M	1.93×10^5	100	1.96×10^{-5}	2.38×10^{-6}	224.2	148.17	3.78×10^{-4}	6.77×10^{-10}
0.2 M	1.93×10^5	200	1.96×10^{-5}	2.46×10^{-6}	223.4	81.28	3.96×10^{-4}	6.65×10^{-10}
0.3 M	1.93×10^5	300	1.96×10^{-5}	2.55×10^{-6}	216.3	75.24	3.85×10^{-4}	6.49×10^{-10}

3.3. Phase compositions and surface microstructures

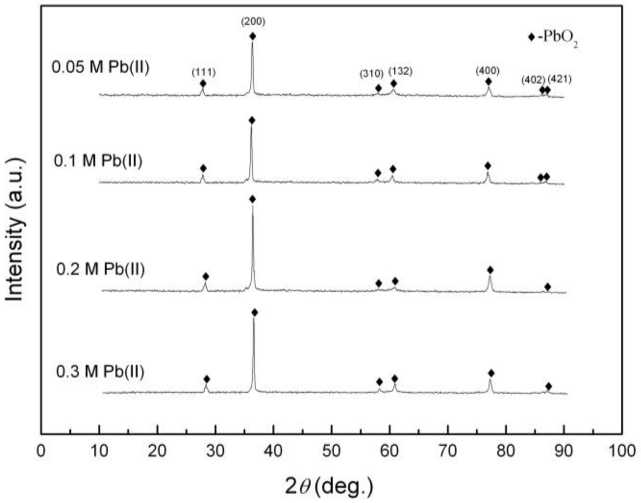

Figure 6. XRD patterns of PbO_2 synthesized on Pt electrode surface in solutions of different Pb(II) concentrations (MSA controlled at 0.1 M).

Fig. 6 shows the XRD patterns of PbO_2 synthesized on Pt electrode surface as a function of the different Pb(II) concentrations at 20°C. The identification of the diffraction peaks was performed and matched with the ICDD Database Card #72-2440. Most of the peaks were identified to the form of PbO_2. We used the Debye-Scherrer equation to estimate the average crystallitesize (Lhkl) of the synthesized PbO_2 from the full width at half maximum height (FWHM) of the peaks at $36.2\,^{o}$ for the various investigated Pb(II) concentrations, just as reported in Table 2. The effect that the grain size increased from 24.5 nm to 31.6 nm as the Pb(II) concentration increased from 0.05 M to 0.2 M and decreased from 31.6 nm to 30.2 nm as the Pb(II) concentration increased from 0.2 M to 0.3 M, which can be attributed to the faster growth of formed nuclei as the apparent heterogeneous rate constant k increased. Equation 4 shows the Debye-Scherrer equation, which is valid for nanosized crystallites.

$$d_g = K\lambda / \beta\cos\theta \qquad (4)$$

where d_g is the crystallite size contribution to the peak width (integral or full width at half maximum) in radians, K is a constant near unity, and β is the average thickness of the crystal.

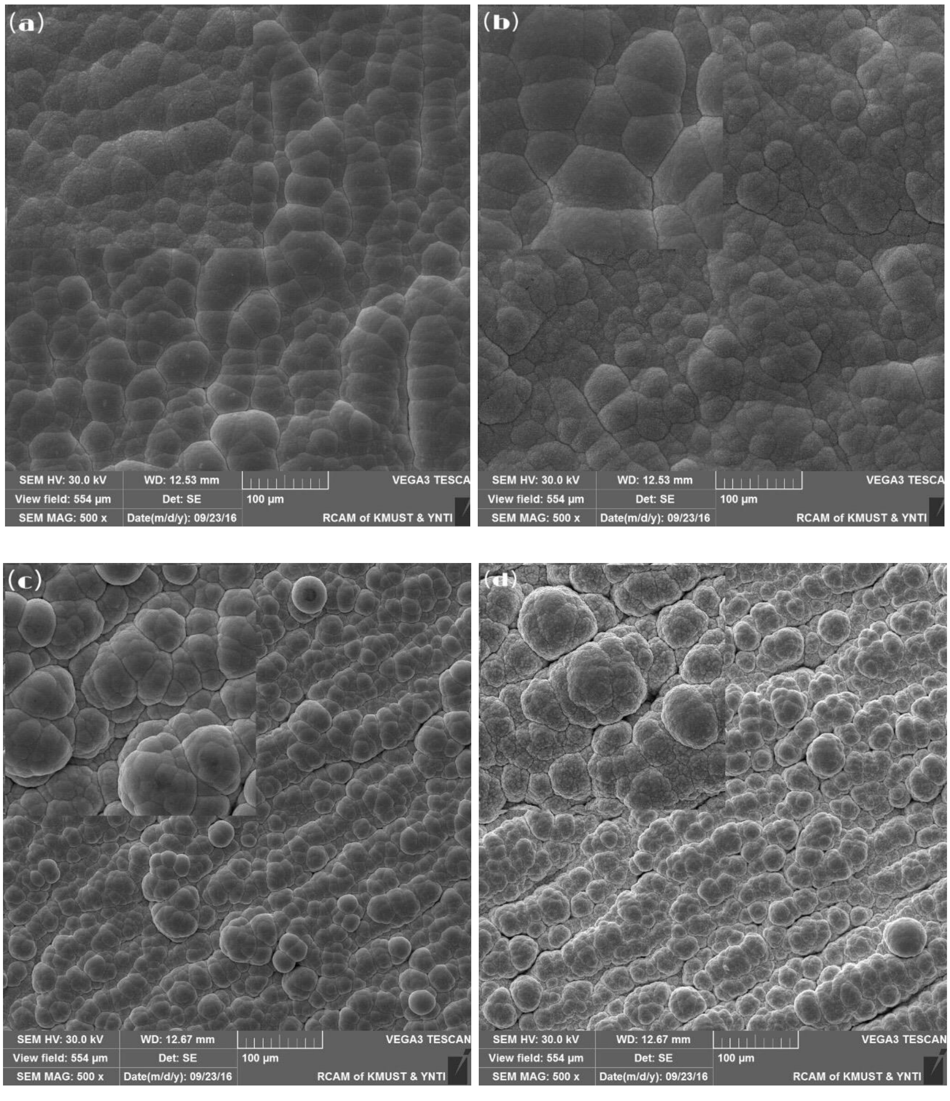

Figure 7. SEM images of PbO_2 synthesized on Pt electrode surface in solutions of different Pb(II) concentrations (MSA controlled at 0.1 M), a: 0.05 M, b: 0.1 M, c: 0.2 M, d: 0.3M.

Table 2. Average size of crystalline grains of PbO_2 synthesized at different Pb(II) concentration.

	Pb(II) concentration of solution/M			
	0.05	0.1	0.2	0.3
d_g / nm	24.5	27.4	31.6	30.2

To assess the influence of the Pb(II) concentration, SEM images of PbO_2 synthesized on the Pt electrode surface in solutions of various Pb(II) concentrations are shown in Fig. 7. It can be seen from the Fig. 7 that the deposit synthesized in the solution with 0.2 M Pb(II) shows longer and finer crystallite compared to the other rounded nanocrystallites deposits. Due to the impact of Pb(II) on the crystallisation of the deposit, many researchers have studied different methods to produce the lead dioxide [48-50]. Di Schino and Kenny reported the impact of the Pb(II) concentration on the deposit in boiling 5 wt% H_2SO_4 solution [51]. Wu also attributed an increase in active dissolution to research the Pb(II) concentration influence [52]. As seen in Fig. 7. a faster apparent heterogeneous rate constants results in a higher electrodeposition rates, indirectly resulting in more orientated crystallites and subsequently yielding the rod-like crystallites until the concentration of the solution increased above 0.2 M. Upon, further increase of the Pb(II) concentration to 0.3 M, a rough substance is observed on the surface of the samples, possibly due to the excess Pb(II) causing the dissolution of PbO_2. In addition, upon the addition of Pb(II), the crystallitesize presents a trend of first increases and then decreases, which is consistent with the average size of crystallite calculated using the Debye-Scherrer equation (Table 2).

4. CONCLUSIONS

In this work, an RDE investigation of the effect of the Pb(II) concentration effect on the electrosynthesis of lead dioxide in MSA was conducted. The following highlights represent the main findings of this work:

(i) We adequately characterised PbO_2 synthesized on a Pt electrode surface, revealing that the Pb(II) concentration has a great influence on the electrodeposition of lead dioxide in environmentally electrolyte of MSA. The reaction taking place at 1.66 V was mixed controlled by ionic transport and charge transfer. The values of the diffusion coefficient D and apparent heterogeneous rate constant k have presented different trends, indicating that Pb(II) has both negative and positive influence on the process of PbO_2 electrodeposition. By controlling the composition of the electrodeposition bath at a Pb(II) concentration of 0.2 M with 0.1 M MSA, we obtained an optimal reversible process, longer electrode lifetime and more satisfactory environmental protection.

(ii) Anodic galvanostatic polarization was used to synthesize the deposits on the Pt surface. The effect of the Pb(II) concentration on the phase composition and surface microstructures of the deposits were observed by XRD and SEM, indicating that compact PbO_2 can be effectively synthesized in a MSA solution. The deposit synthesized under the condition with 0.2 M Pb(II) and 0.1

M MSA showed the preferential orientation of growth along the (200) crystallographic plane and was composed of compact rounded nanocrystallites.

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