An RDE Investigation of NaOH Effect on Electrosynthesis of Lead Dioxide in Alkaline Solution

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Dioxide in Alkaline Solution

An electrochemical investigation of NaOH concentration on electrosynthesis of lead dioxide in alkaline solutions was performed using rotating disk electrodes (RDE). The results show that Pb(II) does not modify the evolution of oxygen in alkaline solutions, and the reaction taking place at 0.84 V_SHE is under the mixed control of ionic transport and charge transfer. The Koutechy-Levich equation was used to calculate the value of diffusion coefficient D and apparent heterogeneous rate constant k of the PbO2 electrodeposition process at 0.84 V_SHE. The results indicate that NaOH has a negative influence on the diffusion of Pb(II) over a NaOH concentration range of 2.5 – 4.5 M. In addition, NaOH has a positive influence on the apparent heterogeneous rate constant k. PbO2 electrodeposition reactions within a NaOH concentration range of 2.5 – 3.0 M, but a negative influence within a NaOH concentration range of 3.0 – 4.5 M. XRD and SEM were employed to investigate the effects of NaOH concentration on phase composition and surface microstructures of deposits. The results show that PbO2 synthesized in an alkaline solution consists of pure α phase. The deposits are all composed of rounded nanocrystals, except for the deposit synthesized in a solution of 3 M NaOH, which exhibited rod-like crystallites.

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Lead dioxide (PbO2) has attracted considerable attention, owing to its low electrical resistivity, low cost, ease of preparation, good chemical stability in acid media, high overpotential for oxygen evolution reactions (OER), and relatively large surface area.1–4 Thus, lead dioxide has already been used in lead batteries,5–7 ozone generation,8,9 and deposition.27,28 It can be used to investigate the kinetics of charge transfer at the electrode/electrolyte interface when paired with a rotating disk electrode (RDE).29–33 The current generated by an electrodeposition process is derived from the chemical process under a given potential gradient.34,35

Experimental

Cyclic voltammetry and rotating disk electrode.—The cyclic voltammetry experiments were carried out using aqueous solutions of Pb(II) and NaOH at different ratios. Alkaline solutions were prepared by dissolving litharge (PbO) in NaOH solution, and the concentration of Pb(II) was controlled at 0.15 M during all experiments. The NaOH concentration changed from 2.5 M to 4.5 M. Analytical grade reagents (AR) and twice-distilled water were used for all solutions. High purity nitrogen gas was purged into the solutions for 20 minutes before applying the potential. All experiments were performed at the temperature of 30°C. A three-electrode system was employed. The working electrode was a Pt RDE (Ametek) with an exposed Pt area of 0.196 cm2 mounted to a rotator. A platinum electrode was the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode. The reference electrode and working electrode were linked by Luggin capillary filled with agar and potassium chloride. In addition, the distance between the capillary and the working electrode surface was about 4 d (d = diameter of capillary). Cyclic voltammetry curves and anodic polarization curves were obtained using an electrochemical workstation (PARSTAT2273). All potentials were given against SHE.

Apparent heterogeneous rate constant and diffusion coefficient.—Values of the apparent heterogeneous rate constants (k) and diffusion coefficients (D) for Pb(II) oxidation were calculated from the linear plots of I−1 versus ω−1/2 according to the Koutecky-Levich equation:

\[ \frac{1}{I} = \left( 0.62nFA\gamma D^{1/2}/\nu C_{0}^{1/2} \right) + \left( nFAC_{0}^{1/2} \right)^{-1} \]  

Where ω is the angular velocity of Pt-RDE (rad/s), C is the bulk concentration of the reacting species (mol/m3), ν is the kinematic viscosity of the solution (m2/s), F is the Faraday constant (C/mol), A is the surface area of Pt-RDE (m2), and n is the effective number of electrons exchanged in the reaction. The rate constants (k) and diffusion coefficients (D) were measured at E = 0.6 V. Kinematic viscosity (ν)
was calculated by the equation:

\[ v = \frac{\mu}{\rho} \]  

where \( v \) is the dynamic viscosity of the solution (Pa · s), and \( \rho \) is the density of the solution (kg/m³). The dynamic viscosity (\( \mu \)) was measured by Brookfield viscometer, and the density was the ratio of mass and volume, which were measured by normal method.

Characterization of surface and phase composition.—The phase composition and surface microstructure characteristics of PbO₂ synthesized on Pt-RDE were measured by D/Max-2200 X-ray diffractometer (XRD) and Nova NanoSEM450 scanning electron microscope (SEM), respectively. The samples were prepared by galvanostatic polarization (10 mA/cm²) in the different solutions. The synthesis time was controlled at 2 h and temperature was 30 °C.

Results and Discussion

Cyclic voltammetry study.—Voltammograms measured in the solution of 2.5 M NaOH + 0.15 M Pb(II) and blank solution (2.5 M NaOH) are shown in Fig. 1. There is only one peak in the blank curve, which can be related to oxygen evolution. All peaks related to the solution containing Pb(II) are referred to with letters. Five main peaks (A to E) can be detected on the curve of the Pb(II)-containing solution. On the anodic branch of the curve, peak C corresponds to the oxygen evolution. Peak A seems to be the process of Pb(II) oxidation, and on the anodic branch of the curve, peak C corresponds to the oxygen evolution. Peak A seems to be the process of Pb(II) oxidation, and the intensity of this range reflects the formation rate of PbO₂.

Rotating disk electrode study.—-Fig. 3 shows the anodic polarization curves of a solution containing different NaOH (Pb(II) controlled at 0.15 M) with a scan rate of 50 mV/s and rotating speeds varying from 400 to 2000 rpm. The five graphs of Fig. 3 show almost identical features. There is no reaction in the potential range of 0.2 ∼ 0.67 V; above 0.67 V the intensity starts to increase; the intensity reaches a stable region at approximately 0.8 ∼ 1.1 V. Some curves for high rotation speeds are disordered in the potential range of 1.2 ∼ 1.5 V. This is because the binding force of PbO₂ and the Pt substrate is not very strong, so the generated PbO₂ exfoliated from the substrate. The measured dependencies of intensity within the stable region are obvious at varying rotation speeds. This result is unambiguous evidence that the transport (mass transfer) of Pb(II) to the electrode surface limits the rate of the electrode process.

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Fig. 4 shows the Koutech-Levich plot obtained at the diffusion plateau (0.84 V) of different NaOH concentrations. The curves indicate that there is direct proportionality between \( I^{-1} \) and \( \omega^{-1/2} \), and the intercept on \( I \) axes is not zero. A result can be drawn that a mixed control (ion transport and kinetics) was present in the reaction taking place at 0.84 V. A curve has been drawn through the points obtained and the goodness of fit of each line is shown in Figure 4. Diffusion coefficient \( D \) has been calculated from the value of the slope using Eq. 1 above. The values of the parameters used in the equation and the results of all calculations are shown in Table 1; all parameters are experimental. It has been assumed that the reaction taking place at 0.84 V is Pb(II) → Pb(IV) (hence \( n = 2 \)). The apparent heterogeneous rate constant \( k \) has also been calculated from the value of the intercept of the fitted line. The diffusion coefficient \( D \) and apparent heterogeneous rate constant \( k \) have an obvious relationship with the NaOH concentration of the solution. The value of diffusion concentration increased. This could be explained by the influence of NaOH concentration on the diffusion of Pb(II). Analysis of Figs. 3 and 4 below confirmed this speculation. The potential of peak B shifted to a more negative potential as the NaOH concentration increased, and it disappeared when NaOH concentration increased to 4 M. The content increase in OH⁻ would promote the oxygen evolution reaction. So peak B shifted to a more negative potential, then was covered by peak A. In the potential range of 1 ∼ 1.4 V, intensities are generally stable. PbO₂ was continuously generated on the electrode in the stable range, and the intensity of this range reflects the formation rate of PbO₂. The RDE investigation below confirmed this speculation. As cathodic peaks, peaks D and E can also reflect the formation weight of the PbO₂ generated in the anodic scan. The intensities of D and E show the same varying pattern as with the intensity of the stable range (1 ∼ 1.4 V).

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Figure 3. Anodic polarization curves of a Pt RDE in solutions of different NaOH concentrations and rotating speeds, (a): 2.5 M NaOH, (b): 3 M NaOH, (c): 3.5 M NaOH, (d): 4 M NaOH, (e): 4.5 M NaOH, Pb(II) controlled at 0.15 M (scan rate, 50 mV/s).
coefficient decreased as NaOH concentration increased, which indicates that NaOH has a negative influence on the diffusion of Pb(II) at an NaOH concentration range of 2.5 ~ 4.5 M. The intensity change of Peak A in Fig. 2 may also reflect the difficulty of Pb(II) diffusion in alkaline solutions. In addition, the value of rate constant $k$ increased at first, then decreased as the NaOH concentration increased from 2.5 M to 4.5 M. The rise in rate constant from 2.5 ~ 3 M (NaOH concentration) could be explained by Formula 3, while the increase in $\text{OH}^-$ concentration can promote the reaction shown in Formula 3 to-ward positive.\textsuperscript{38,39} However, a further increase in NaOH concentration (>3 M) would also promote the reaction of oxygen evolution, and excess $\text{OH}^-$ may adsorb onto the surface of the electrode waiting to be polarized. The process of PbO$_2$ electrodeposition on the surface of RDE is shown in Fig. 5.

$$\text{HPbO}_2^+ + \text{OH}^- \rightarrow \text{PbO}_2 + \text{H}_2\text{O} \quad [3]$$

Phase compositions and surface microstructures.—The XRD patterns of PbO$_2$ synthesized on Pt electrode surface in solutions of different NaOH concentrations are shown in Fig. 6. XRD analysis confirms that PbO$_2$ synthesized in an alkaline solution consists of pure $\alpha$ phase matching the ICDD Database Card #72-2440. However, not all characteristic peaks are present and relative intensities are not in agreement with the ICDD card, which was also observed by R. Ingualta.\textsuperscript{41} A preferential orientation of growth in the (200) crystallographic plane can easily be observed, and the $\alpha$-PbO$_2$ deposit is polycrystalline. The intensity of other crystallographic planes is much lower compared to (200). The intensity of the (200) crystallographic plane initially increased along with the NaOH concentration (<3 M), then decreased when NaOH concentration exceeded 3 M, which shows the same variation of the calculated apparent heterogeneous rate constant $k$. This indicates that increases in the apparent heterogeneous rate constant $k$ would promote $\alpha$-PbO$_2$ toward the (200) crystallographic plane. Moreover, the (400) and (421) crystallographic planes almost disappeared in the XRD pattern of the sample obtained from the 3 M NaOH solution. The average crystallite size (Lhkl) of synthesized $\alpha$-PbO$_2$ was estimated from the full width at half maximum height (FWHM) of the peaks at 36.2.\textsuperscript{23} The Debye-Scherrer equation, which is valid for nanosized crystallites, was employed in the estimation, and the values obtained at investigated NaOH concentrations are reported in Table II. It can be observed that grain size increased from 34.3 nm to 40.4 nm as NaOH concentration of the original plating bath increased from 2.5 M to 3 M. In addition, the grain size decreased from 40.4 nm to 30.9 nm as NaOH concentration of the original plating bath increased from 3 M to 4.5 M. This effect can be attributed to the faster growth of formed nuclei as apparent heterogeneous rate constant $k$ increases.

In order to assess the influence of NaOH concentration, the microstructure of deposited samples was also characterized by SEM. Fig. 7 shows the SEM images of PbO$_2$ synthesized on Pt electrode surface in solutions of varying NaOH concentrations. As can be seen, compact deposits were obtained with alkaline solutions, but the general morphological trends occurred when varying NaOH concentration. The deposits are all composed of rounded nanocrystallites, except for the deposit synthesized in the solution of 3 M NaOH, of which its crystallite is longer and finer than any other deposits. This phenomenon can be due to the highest intensity of the (200) crystallographic plane of XRD pattern of deposit obtained in 3 M NaOH solution and the highest apparent heterogeneous rate constant $k$ of 3 M NaOH solution obtained in part 3.2. Higher apparent heterogeneous rate constants involve higher electrodeposition rates, and higher electrodeposition rates may lead to more orientated crystallization, subsequently yielding the rod-like crystallite. The uniformity of crystallites starts to decrease as concentration of the solution increased to greater than 3 M, and there was detected a flake-like substance on the surface of the samples obtained from solutions containing 4 M and 4.5 M NaOH. One possible explanation is that PbO$_2$ is very soluble in strongly alkaline solutions, with the resulting formation of plumbate ions PbO$_2$$^{-}$\textsuperscript{42} In addition, the crystallite size initially increased and subsequently decreased as NaOH concentrations increased, which can be observed in Fig. 6, confirming the average size of crystallite calculated using the Debye-Scherrer equation (Table II).

### Conclusions

In this study, the effects of NaOH concentration were investigated by cyclic voltammetry and rotating disk electrode techniques in order to study the electrodeposition process affected by NaOH. The presence of Pb(II) did not modify the evolution of oxygen in alkaline solutions, and the reaction taking place at 0.84 V was under the

| NaOH Concentration | Intercept | Slope | $k$(m/s) | $D$(m$^2$/s) |
|--------------------|-----------|-------|----------|--------------|
| 2.5 M              | 3.64 28   |       | 3.63E-04 | 9.68E-10     |
| 3 M                | 3.64 28   |       | 5.34E-04 | 7.36E-10     |
| 3.5 M              | 4.36 26   |       | 4.93E-04 | 6.81E-10     |
| 4 M                | 524.72    |       | 4.46E-04 | 5.77E-10     |

### Table I. Verification of Koutecky-Levich equation.

| NaOH Concentration | $nF(C/mol)$ | $C$(mol/l$^3$) | $A$(m$^2$) | $v$(m$^2$/s) | Intercept | Slope | $k$(m/s) |
|--------------------|-------------|----------------|------------|--------------|-----------|-------|----------|
| 2.5 M              | 1.93E + 05  | 150            | 1.96E-05   | 4.03E-06     | 4.86      |       | 3.63E-04 | 9.68E-10 |
| 3 M                | 1.93E + 05  | 150            | 1.96E-05   | 4.08E-06     | 3.3       |       | 5.34E-04 | 7.36E-10 |
| 3.5 M              | 1.93E + 05  | 150            | 1.96E-05   | 4.26E-06     | 3.58      |       | 4.93E-04 | 6.81E-10 |
| 4 M                | 1.93E + 05  | 150            | 1.96E-05   | 4.42E-06     | 3.95      |       | 4.46E-04 | 5.77E-10 |
| 4.5 M              | 1.93E + 05  | 150            | 1.96E-05   | 4.69E-06     | 4.1       |       | 4.30E-04 | 5.07E-10 |
mixed control of ionic transport and charge transfer. The values for diffusion coefficient $D$ and apparent heterogeneous rate constant $k$ of the electrodeposition process at 0.84 V were calculated using the Koutecky-Levich equation. The value of the diffusion coefficient decreased as the NaOH concentration increased, indicating that NaOH has a negative influence on the diffusion of Pb(II) within a NaOH concentration range of 2.5 $\sim$ 4.5 M. In addition, the value of the apparent heterogeneous rate constant increased at first, then decreased as the NaOH concentration increased from 2.5 M to 4.5 M. The deposits were successfully synthesized on the Pt surface via anodic galvanostatic polarization in alkaline solutions. XRD and SEM were employed to investigate the effects of NaOH concentration on phase composition and surface microstructures of deposits. The results confirmed that PbO$_2$ synthesized in an alkaline solution consists of pure $\alpha$ phase. The preferential orientation of growth along the (200) crystallographic plane can be observed on the XRD patterns of $\alpha$-PbO$_2$ deposits. The intensity of the (200) crystallographic plane initially increased with the rise in NaOH concentration ($<3$ M), then decreased when the NaOH concentration exceeded 3 M, which shows the same variation for the calculated apparent heterogeneous rate constant $k$. The average crystallite size of deposits obtained from solutions with NaOH concentrations from 2.5 $\sim$ 4.5 M changed from 30.9 nm to 40.4 nm; these values were calculated using the Debye-Scherrer equation. The deposits were all composed of rounded nanocrystallites, except for the deposit synthesized in the solution of 3 M NaOH, which exhibited rod-like crystallite.

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