BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1889—1890 (1977)

Polarographic Catalytic Currents Observed in Mixtures of Pb(II) and H_2O_2 in Neutral Solutions

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(Received January 13, 1977)

Synopsis. Normal pulse polarography has shown that the catalytic wave observed in neutral mixtures of Pb(II) and H_2O_2 is caused by $Pb(OH)^+$ at the electrode surface, and that OH^- ions are liberated in the vicinity of the electrode due to the catalytic reaction.

It was first noticed by Strnad that traces of Pb(II) ions in neutral air-saturated solutions greatly increased the first oxygen wave.[1] This effect of Pb(II) ions was explained as being due to the reduction of H_2O_2 arising from the reduction of oxygen.

This paper will describe the results of a polarographic investigation of the Pb(II)–H_2O_2 system.

Apparatus and Reagents

Apparatus. The polarograms were obtained with a PAR (Princeton Applied Research) Polarograph, Model 174. The polarograms were recorded on a Riken Denshi X-Y Recorder, Model D-8C. The dropping mercury electrode (DME) used had a $m^{2/3}t^{1/6}$ of 1.45 $mg^{2/3}s^{-1/2}$ in 0.1 M KNO_3 in an open circuit. The drop time of the DME was controlled at 1.0 s by means of a Mechanical Drop Time Controller, Model 172-A. The pH values of the test solutions were measured with a Hitachi-Horiba pH Meter, Model M-7. A saturated calomel electrode (SCE) was used as the reference electrode. The solutions were deoxygenated by bubbling nitrogen gas through them. All the experiments were carried out at (25±0.1)°C.

Reagents. All the chemicals were of a reagent grade and were used without further purification.

Results and Discussion

Figure 1(A) shows the effect of the pH on the DC polarogram of 1.0 mM Pb(II) in 0.1 M $NaNO_3$ without dissolved oxygen. When pH <5, a single wave was observed with a half-wave potential of —0.38 V. As the pH was increased, the wave split into two waves, the relative heights being pH-dependent. When pH >8.5, the first wave disappeared and only the second one remained.

Figure 1(B) shows the percentage distribution curves calculated from the data[2] for the four possible species present in Pb(II) solutions. The observed dependence of the relative wave heights on the pH corresponds to the changing ratio of the aquated Pb(II) ion to the hydroxide species. Therefore, the first wave is ascribed to the reduction of the aquated Pb(II) ion, and the second, to the reduction of $Pb(OH)^+$.

Figure 2 illustrates DC polarograms of 0.4 mM Pb(II) in 0.1 M $NaNO_3$ (pH 4.6) containing 5 mM H_2O_2. The catalytic wave was observed in unbuffered solutions in the pH range of 4—8 (Curve a).

The polarographic behavior of the Pb(II) ion in buffered solutions of various pH values was also investigated. When the pH was adjusted with either an acetate or barbital buffer to lie in the range of 4—5, where $Pb(OH)^+$ did not exist to any appreciable extent in the solution, no catalytic wave appeared (Curve b in Fig. 2). However, in either a borate or barbital buffer with a pH of about 7.5 (in the pH region where $Pb(OH)^+$ exists), the catalytic wave appeared.

Normal pulse polarography was applied to elucidate a catalytically active Pb(II) species. Figure 3 shows normal pulse polarograms of 1.0 mM Pb(II) in 0.1 M $NaNO_3$ (pH 4.8) containing various concentrations of H_2O_2. With the H_2O_2 concentration of 2 mM, the initial single wave split into three waves. Above this

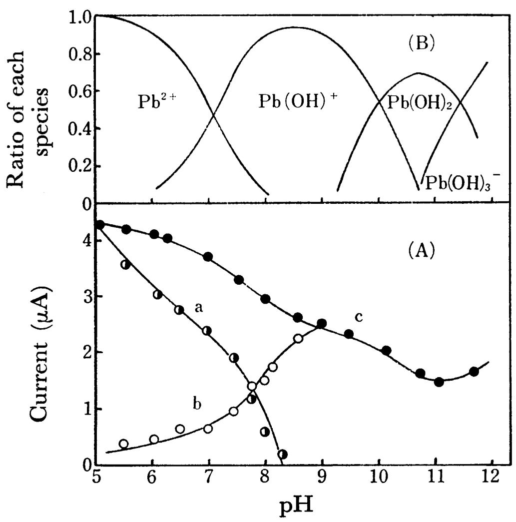

Fig. 1(A). Effect of pH on DC polarographic wave of 1.0 mM Pb(II) in 0.1 M $NaNO_3$ without dissolved oxygen.

a) 1st wave. b) 2nd wave. c) Total wave.

Fig. 1(B). Effect of pH on the ratio of four Pb(II) species.

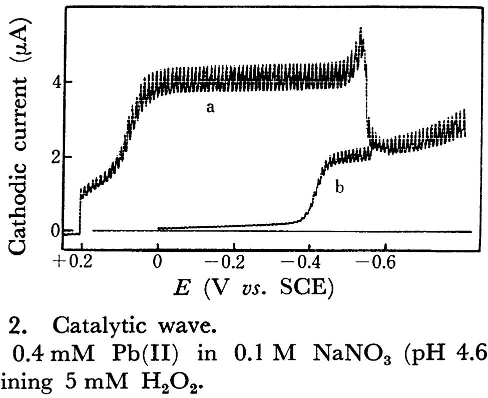

Fig. 2. Catalytic wave.

a) 0.4 mM Pb(II) in 0.1 M $NaNO_3$ (pH 4.6) containing 5 mM H_2O_2.

b) Solution (a) with acetate buffer (pH 4.6).

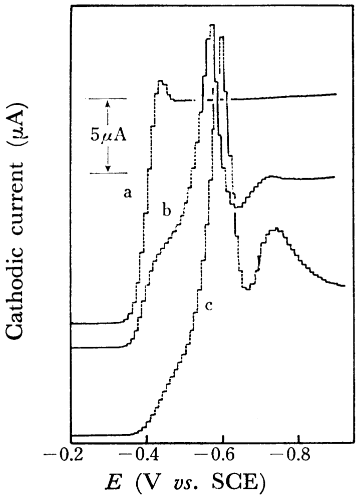

Fig. 3. Normal pulse polarograms of 1.0 mM Pb(II) in 0.1 M $NaNO_3$ (pH 4.8) containing various concentrations of H_2O_2. H_2O_2 concentration (mM) a) 0. b) 2.0. c) 3.0. $E_i = -0.2$ V.

H_2O_2 concentration, the first wave disappeared with an increase in the height of either the second or the third one.

To identify the Pb(II) species responsible for each wave, normal pulse polarograms in unbuffered solutions containing 1 mM Pb(II) and dissolved oxygen were also recorded. When the initial potential was set at +0.3 V, which was more anodic than the reduction potential of the first oxygen wave, the normal pulse polarogram of Pb(II) had two reduction waves. The first wave was interpreted as being due to the reduction of the aquated Pb(II) ion, and the second, to the reduction of $Pb(OH)^+$, the behavior of which was analogous to that observed in DC polarography. When the initial potential was set at −0.2 V, where the reduction of oxygen took place, the normal pulse polarogram consisted of three waves similar to Curve (b) of Fig. 3. Under these conditions, the concentration of OH^- ions increases in the vicinity of the electrode at the initial potential because of the reduction of the oxygen.

By buffering the solution, either the second or the third wave disappeared completely and the first wave became well defined.

As has been reported previously,[3,4] $Ni(OH)_2$ and $Fe(OH)_2$ produced similar waves on a normal pulse polarogram under the same conditions. Similarly, the third wave reflects the reduction of the $Pb(OH)_2$ formed at the electrode surface.

By analogy with the system composed of Pb(II) and dissolved oxygen, it is conculded that the first wave of Fig. 3(b) corresponds to the reduction of the aquated Pb(II) ion, and that the two remaining waves are due to the reduction of $Pb(OH)^+$ and $Pb(OH)_2$. This means that the catalytic reaction between Pb(II) and H_2O_2 proceeds with the formation of OH^- ions in the vicinity of the electrode.

Figure 4 shows the effect of the pH on the normal pulse polarogram of 1.0 mM Pb(II) in 0.1 M $NaNO_3$ containing 5 mM H_2O_2. Clearly, under the conditions where the catalytic reaction occurs, the aquated Pb(II) ion does not exist in the solution, and the region where $Pb(OH)^+$ is present is about from pH 4 to 8, this range agreeing with that where the catalytic wave appears in DC polarography.

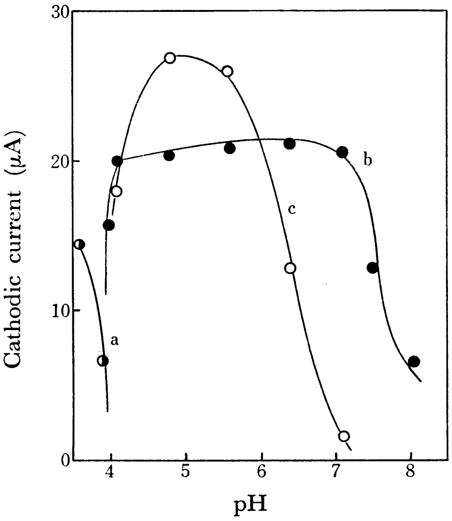

Fig. 4. Effect of pH on normal pulse polarographic wave of 1.0 mM Pb(II) in 0.1 M $NaNO_3$ containing 5 mM H_2O_2.
a) lst wave. b) 2nd wave. c) 3rd wave.
$E_i = -0.2$ V.

As is shown in Fig. 2, the catalytic current drops at −0.55 V, which is about 0.17 V more negative than the reduction potential of the aquated Pb(II) ion. This result also indicates that the aquated Pb(II) ion is converted to $Pb(OH)^+$ as a result of the catalytic reaction. This is inconsistent with the work of Strnad, who explained the current drop in terms of the direct reduction of the aquated Pb(II) ion to Pb(0).

The most likely mechanism for the catalytic reaction is that $Pb(OH)^+$ is oxidized by H_2O_2 to the Pb(IV) ion, which is then rapidly reduced at DME to produce a catalytic wave. Traces of $Pb(OH)^+$ may cause the catalytic reaction in unbuffered solutions in the pH range of 4—5. An increase in $Pb(OH)^+$ at the electrode surface is necessary for the catalytic reaction to proceed under these conditions.

The author wishes to thank Professor Atsuyoshi Saito for his valuable advice and for his helpful discussions throughout this study.

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