B. Electrochem 4(4) April 1988, pp 351-354

EQUILIBRIUM POTENTIAL OF ß-PbO_2 IN NITRATE SOLUTION

K. C. NARASIMHAM
Central Electrochemical Research Institute, Karaikudi-623006, INDIA

[Received: 1987 July; Accepted: 1988 February]

During tshe examination of the final state of the reaction on the electrochemical kinetics, it has become essential to study the duration needed for the ß-lead dioxide to attain equilibrium potential in nitrate solution. This was studied by first depositing ß-lead dioxide on platinum foil from 1M lead nitrate solution using a H-type cell and introducing freshly prepared anodes (for each experiment) in the experimental cell containing deaerated lead nitrate solution. The potential measurements were carried out against saturated calomel electrode (SCE) and at a temperature of 303 + 0.2 K for 60 minutes. The variation of equilibrium potential with time was studied for (i) ß lead dioxide prepared for different durations (ii) different concentrations of lead nitrate and (iii) different nitric acid concentrations. The buffering action was also seen by taking lead acetate in acetic acid. In general, the equilibrium potential for ß- PbO_2 is quickly attained in acidic solutions. It is known that lead dioxide behaves as a non-stoichiometric oxide electrode and the variations in the deviations from the ideal stoichiometry. The variation of equilibrium potential with time is discussed taking into consideration of these facts.

Key words: Equilibrium potential, lead dioxide, lead nitrate electrolyte

INTRODUCTION

The formation of metallic oxides by the anodic oxidation of solutions of the salts of the metals is a group of reactions of considerable interest, as the process may be studied from a variety of solutions. Most of these oxides exist in two or more modifications. The anodic oxidation of plumbous salts can be considered as one of the examples of these reactions. The lead dioxide electrodes prepared by electrodeposition of the oxide, preferably, from nitrate baths are used as anodes for a variety of inorganic and organic oxidation reaction [1]. Hence the electrochemical kinetics of the anodic oxidation of plumbous salts is of major interest.

During the examination of the final state of the reaction on the electrochemical kinetics, it has become necessary to study the duration needed for the ß-lead dioxide to attain equilibrium potential in nitrate solution. This paper deals with the measurement of equilibrium potential of ß-lead dioxide in nitrate solution. The lead dioxide is treated from' the kinetic point of view as a non-stoichiometric oxide electrode [2-5]. Although kinetic studies have been carried out in different electrolytes [6,7], not much studies have been done in nitrate medium.

EXPERIMENTAL

Cell assembly

A 250 ml round bottom pyrex flask fitted with an outer jacket carrying water circulated under thermostatic control to maintain the temperature of the electrolyte, was used as the cell. This was provided with a three-necked cover for introducing the working electrode, Luggin capillary and gas inlet. To avoid the mixing of potassium chloride with lead nitrate (when lead chloride would precipitate), two bridges were provided with ammonium nitrate solution in the middle. A saturated calomel electrode (SCE) dipping in potassium chloride was used as a reference electrode.

Working electrode

A platinum foil (1 cm x 1.4 cm) was cleaned by dipping in nitric acid (1:1), washed well with distilled water and conductivity water. Lead dioxide was deposited on the foil from 1M-lead nitrate solution (in some experiments different electrolytes were used) using a H-type cell with a sintered disc in the horizontal limb to separate the anode and cathode compartments. The cathode was also a platinum sheet (1 cm wide x 5 cm long). A constant current generator (with less than 1% a.c.ripple) was used as the D. C. source and the deposition was carried out at anode current density of 20 mA. cm^{-2} and a temperature of 302 ± 1 K. The deposition was carried out for 15 minutes in all the experiments except in the experiments carried out with different durations of deposition. After the deposition, the electrode was washed well with conductivity water and kept in a desiccator for 10 minutes before being introduced in the electrolyte for measuring the equilibrium potential.

Electrolyte

Different concentrations of lead nitrate solution were prepared by dissolving required weight of recrystallised lead nitrate in conductivity water and made up to required volume. When lead acetate was used similar procedure was adopted.

Measurement

After arranging the cell assembly, the electrolyte was taken in the cell and deaeration was done by bubbling pure nitrogen. The working electrode was introduced and the variation in potential (vs SCE) was measured with time for 60 minutes. During the potential measurements, nitrogen gas was not bubbled into the electrolyte. All the experiments were conducted at a temperature of 303 ± 0.2 K.

RESULTS

Fig.1 Shows the variation of equilibrium potential with time in 1M lead nitrate solution for ß-lead dioxide prepared for different durations. It can be seen from the figure that even though the open

0256-1654/88/$ 3-50/© 1988 CECRI

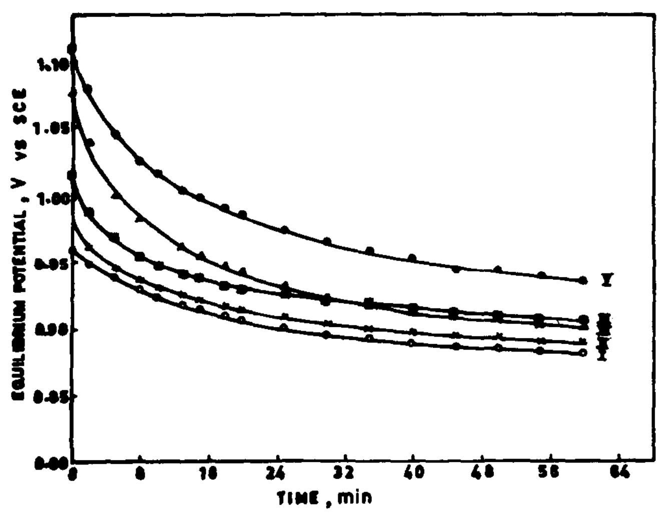

Fig. 1: Variation of equilibrium potential with time in 1M $Pb(NO_3)_2$ solution for ß- PbO_2 prepared for different durations I = 5 min: II = 10 min; III = 15 min; IV = 30 min: V = 60 min.

circuit potential increases at electrodes prepared for longer durations, the final potentials for the electrodes with 15 minutes and 30 minutes remain almost constant. Hence for further experiments, deposition of ß-lead dioxide was carried out only for 15 minutes.

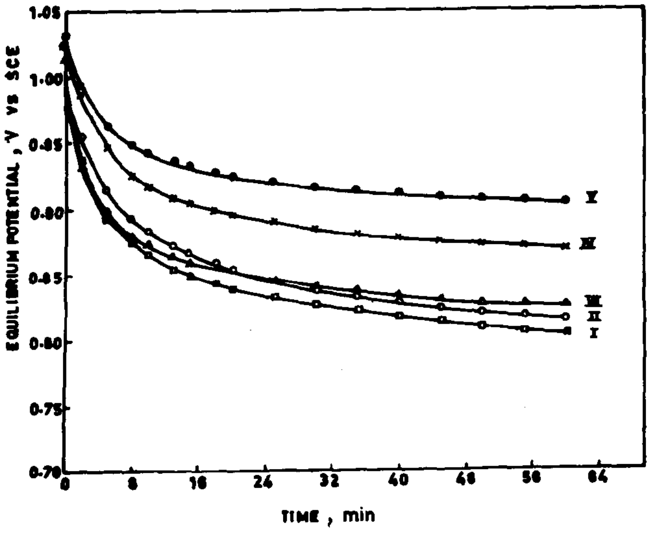

Fig. 2: Variation of equilibrium potential in different concentrations of $Pb(NO_3)_2$ solution
I = 0.01M (pH = 4.95); II = 0.05M (pH = 4.55); III = 0.1M (pH = 4.40); IV = 0.05M (pH 3.95); V = 1.0M (pH 3.7)

The variation of equilibrium potential of ß-lead dioxide in different concentrations of lead nitrate is shown in Fig. 2, which clearly shows that the final equilibrium potential value at 60 minutes increases with increase in concentration while the difference is small (less than 10 mV) for concentrations of 0.01M to 0.1M, the difference is between 30-50mV for higher concentrations.

To study the effect of acid on the equilibrium potential, experiments were conducted with ß-lead dioxide in lead nitrate solution containing nitric acid and the results are graphically represented in Fig 3. It is seen that the equilibrium is attained quickly in acidic solutions, though the potential is higher in the same. However, the deposit obtained from acidic solutions does not attain the equilibrium so quickly in lead nitrate solution. The final equilibrium potential after 30 minutes is higher by 50 mV from that of the electrode prepared from pure lead nitrate solution containing no acid.

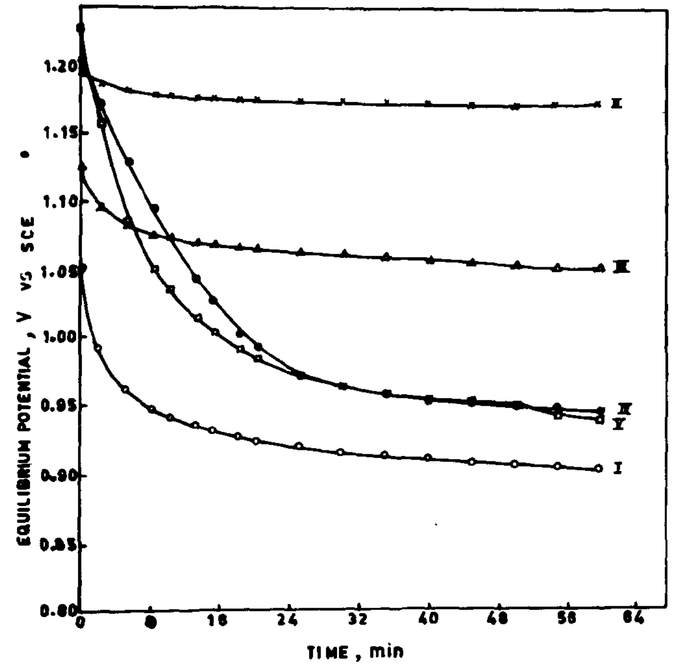

Fig. 3: Effect of acid on the equilibrium potential for ß- PbO_2 deposited from 1M $Pb(NO_3)_2$
I = 1M $Pb(NO_3)_2$; II = 1M $Pb(NO_3)_2$ + 0.01M HNO_3; III = 1M $(PbNO_3)_2$ + 0.1M HNO_3; IV = for ß-PbO_2 deposited from 0.515M $Pb(NO_3)_2$ + 2M HNO_3 and V = for ß- PbO_2 deposited from 0.1M $Pb(NO_3)_2$ + 2M HNO_3 (Eq.potential in 1.0 M Pb $(NO_3)_2$ solution for IV and V)

The buffering action was also seen by taking lead acetate [7,8]. The results (Fig. 4) indicate that the equilibrium potential is lower in acetate solution than in nitrate solution. However the deposit obtained from lead acetate solution shows a marked increase in potential (~60 mV) in lead nitrate solution, whereas the increase is marginal in lead acetate solution.

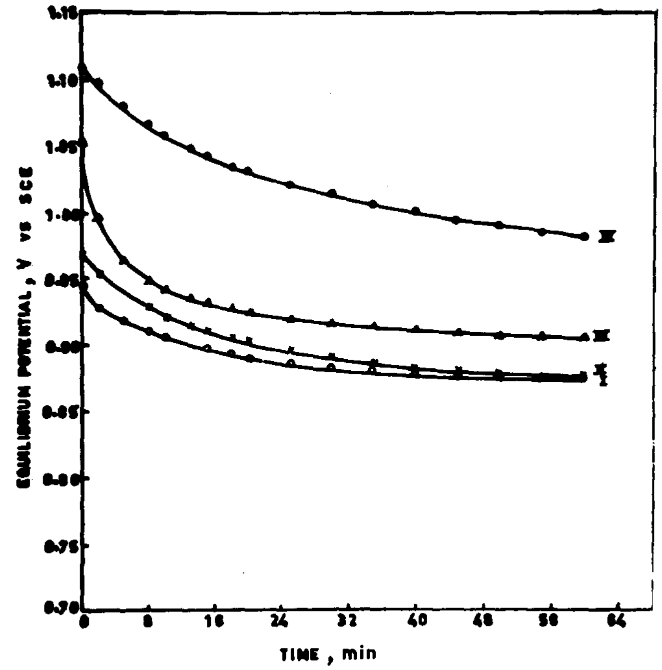

Fig.4: Effect of lead acetate on the equilibrium potential
A = Potential in 1M $Pb(Ac)_2$ solution PbO_2 deposited from:
I = 1M Pb $(NO_3)_2$; II = 1M $Pb(Ac)_2$ solution;
B = Potential in 1M $Pb(NO_3)_2$ solution; PbO_2 deposited from:
III = 1 M-Pb $(NO_3)_2$; IV = 1M $Pb(Ac)_2$

DISCUSSION

It is known that lead dioxide behaves as a nonstoichiometric oxide electrode and the variations in chemical potentials of lead and of oxygen are related to the deviations from the ideal stoichiometry [5]. The electrodeposited lead dioxide whose composition can be represented as Pb $O_{(2-\delta)}$ $(x.H_2O)$ can function as lead electrode with variable chemical potential of Pb in PbO_2, as oxygen electrode with variable chemical potential of O_2 in PbO_2 and as hydrogen electrode [9].

$$E_{PbO_2} / V = 1.449 - 0.0295 \log a_{Pb^{2+}}(aq) - 0.118 \text{ pH} \quad \ldots (1)$$

$$E_{O_2} / V = 1.229 + 0.0148 \log (p_{O_2} / p^{\circ}_{O_2}) - 0.059 \text{ pH} \quad \ldots (2)$$

$$E_{H_2} (PbO_2) = E^{\circ}_{H_2} - \frac{RT}{2F} \ln a_{H_2} (PbO_2) + \frac{RT}{F} \ln a_{H^+} (aq) \quad \ldots (3)$$

At equilibrium

$$E_{Pb} (PbO_2) = E_{O_2} (PbO_2) = E_{H_2}(PbO_2) = E_{PbO_2} \quad \ldots (4)$$

The deviation from ideal stoichiometry viz δ is a variable quantity and that the $(x.H_2O)$ indicates available amount of water dissolved in PbO_2. Water or hydrogen exists in the solid PbO_2 phase and has been confirmed by NMR studies [10,11] as well as by electrochemical methods[12].

It is further reported [9] that the partial pressure of oxygen in PbO_2 which is in equilibrium with an electrolyte depends on the thermodynamic activities of Pb^{2+} and H^+ in the solution. p_{O_2} (PbO_2) varies with the changing composition of the electrolyte. The deviation δ from the ideal stoichiometry of $P_{O_2}$is a function of chemical potential of O_2 in $PbO_{(2-\delta)}(x.H_2O)$ or as a function of the equilibrium partial pressure of oxygen in the oxide p_{O_2} (PbO_2).

If PbO_2 is in equilibrium with the given electrolyte containing Pb^{2+}, the chemical potential of PbO in PbO_2 is fixed by the equilibrium in solution:

$$\mu_{PbO} [PbO_2] = \mu_{PbO} \text{ (electrolyte)} \quad \ldots (5)$$

Even if PbO cannot be found in the form of undissociated PbO molecule, it may be built up in the electrolyte according to the following reaction [9].

$$PbO = Pb^{2+} (aq) + H_2O - 2H^+ (aq) \quad \ldots (6)$$

The deposition or dissolution of PbO and/ or $Pb(OH)_2$ changes the stoichiometry of $PbO_{(2-\delta)}$ $(x. H_2O)$, which is the case when lead dioxide electrode is currentless but not in equilibrium with the surrounding solution.

The change in stoichiometry of PbO_2 may be explained to a large extent by the deposition or dissolution of H_2 into or out of PbO_2. It has also been reported [9] that the interstitial protons existing in PbO_2 are the disorder centres. When PbO_2 is exposed to air for several days, a desorption of oxygen or an absorption of hydrogen has been observed [13], which has been related to the increase of electron concentration. The incorporation of O_2 or H_2 into lattice occurs as per the following reactions [14]

$$O_2 + 2 V_o^{\bullet\bullet} + 4e \longrightarrow 2 O_o \quad \ldots (7)$$

$$2H_2O + 4 V_i \longrightarrow 4 H_i^{\bullet} + 4e + O_2 \quad \ldots (8)$$

where $V_o^{\bullet\bullet}$is oxygen vacancy, O_o = oxygen at oxygen site in the lattice, V_i = empty interstitial site, H_i = interstitial proton and e = quasi - free electron in PbO_2.

In addition, it is also suggested [3,4,] that PbO_2 can be considered not only as a Pb electrode or O_2 electrode but also H_2 electrode since hydrogen is dissolved in PbO_2. The dissolution of lead and $H_2$from PbO_2 and incorporation of O_2 can be according to the following reactions [9]:

$$Pb(\text{in } PbO_2) = Pb^{2+}(aq) + 2e \ (\text{in } PbO_2) \quad \ldots (9)$$

$$H_2O = O \ (\text{in } PbO_2) + 2H^+ (aq) + 2e \ (\text{in } PbO_2) \quad \ldots (10)$$

$$H \ (\text{in } PbO_2) = H^+ (aq) + e \ (\text{in } PbO_2) \quad \ldots (11)$$

Thus it can be said that the initial decrease of potential in these experiments is due to removal of PbO as given in eq(6). The equilibrium potential increases with decreasing pH, which is due to variation of partial pressure of oxygen and depends on the thermodyanamic activities of Pb^{2+} and H^+ in the solution as per the following equation[9].

$$\log p_{O_2}(PbO_2) = \text{Const.} -2 \log a_{Pb^{2+}(aq)} + 4\log a_{H^+(aq)} \quad ..(12)$$

The oxygen electrode potential is thus dependent on partial pressure of oxygen (vide eq.2). The higher equilibrium potential is thus due to increase in oxygen electrode potential.

Acknowledgement: The author wishes to express his sincere thanks to Dr V.K Venkatesan, Deputy Director of the Institute for useful discussions.

REFERENCES

1. K C Narasimham and H V K Udupa, *J Electrochem Soc* 23 (1976) 1294
2. W Fischer and H Rickert, *Ber Bunsenges Physik Chemie,* 77 (1973) 975
3. H Rickert, *Z Phys Chem* (Frankfurt Au. Main), 95 (1-3) (1975) 47
4. J. P Pohl and H Rickert, *Ibid,* 95 (1-3)(1975)59
5. J P Pohl and H Rickert, in (Ed) D H Collins, *Power Sources,* Academic Press, London (1976) p 59
6. J P Carr and N A Hampson, *Chem Rev* 72 (1972) 679
7. M Fleischmann and M Liler, *Trans Faraday Soc,* 54 (1958) 1370
8. S Vasundara, K C Narasimham and H V K Udupa, *Electrochim Acta,* 16 (1971) 1301
9. J P Pohl and H Rickert in (Ed) s Trassati, *Electrodes of conductive metallic oxides-Part B,* Elsevier Publishing Co., Amsterdam (1981) p 186
10. S M Caulder, J S Murday and A C Simon, *J Electrochem Soc,* 120 (1973) 1515
11. S M Caulder and A C Simon, *J Electrochem Soc,* 121 (1974) 1546
12. J P Pohl and H Rickert in (Ed) S. Trassati, *Electrodes of conductive metallic oxides-Part B,* Elsevier Publishing Co. Amsterdam (1981) p 211
13. W Mindt, *J Electrochem Soc,* 116 (1969) 1076
14. F A Kroger, *The chemistry of imperfect crystals,* North Holland, Amsterdam (1964)