In-Situ Spectroelectrochemical Studies of Manganese(II)
Oxidation

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Abstract: *In-situ* spectroelectrochemical studies have been carried out on the oxidation of Mn(II) at platinum, gold, lead dioxide, and bismuth doped lead dioxide electrodes. The Mn(III), MnO_2, and/or MnO_4^- species are produced depending on experimental conditions employed during electrolysis. Mn(III) is shown to be produced from a very early stage during the anodic potential scan and undergo disproportionation-conproportionation reactions depending on the relative concentration of each species near the electrode surface. An oxidation mechanism consistent with these observations is proposed.

Keywords: Oxidation Mechanism, Mn(II), Mn(III), permanganate

1. Introduction

The electrochemical oxidation of manganese (II) produces a few different products including Mn(III), MnO_2, and Mn(VII) depending on experimental conditions employed. Mn(III) and Mn(VII) are strong oxidants, both of which have been used as titrants in analytical chemistry. Due to the importance of the oxidation reaction, numerous experiments have been carried out on the subject [1-24]. Selim and Lingane [6] reported that Mn(III) can be stabilized by complexion with SO_4^{2-} in the presence of an excess of Mn(II).

However, Dienbler and Sutin [7], Rosseinsky [8], and Wells and Davies [9] claimed that Mn(III) can be stabilized in the perchlorate solution, which is not a complexing medium for Mn(III). They also reported the spectrum of Mn(III) in perchlorate solutions. A review is available on the subject [10]. Recently, Randle and Kuhn have studied the oxidation of Mn(II) to Mn(III) at platinum [11] and PbO_2 [12] electrodes. Boardman *et al.* [22] and Comninellis and Petitpierre [23] discussed catalytic activities of Ag(I) during the oxidation of Mn(II) to MnO_4^-. Johnson's group reported a series of studies on the oxidation of Mn(II) at PbO_2 and bismuth-doped PbO_2

electrodes to generate and use MnO_4^- for oxygen-transfer reactions [24-27]. Their studies indicate that the bismuth doped PbO_2 electrode shows a catalytic effect on the oxidation process [24].

In this study, we report the rsults obtained from the electrochemical oxidation of Mn(II) in 1 M $HClO_4$ solutions. *In-situ* spectroelectrochemical methods have been used to study the effects of concentrations of manganese (II), initial potentials, electrode materials, and scan rates on its oxidation.

2. Experimental

Mn(II) solutions of various concentrations used in this study were prepared using manganous sulfate in 1 M $HClO_4$. Mn(III) solutions were made by adding a given amount of $KMnO_4$ to an excess of Mn(II) in 1 M $HClO_4$ solution. It has been well established that MnO_4^- oxidizes Mn(II) to Mn(III) quantitatively under this condition [10].

Platinum, PbO_2, or bismuth doped PbO_2 (Bi-PbO_2 in short) electrodes were used as working electrodes. The PbO_2 electrode was prepared by depositing the oxide film on platinum foil or gold disk electrodes from a 1 mM $Pb(NO_3)_2$ solution in 1 M $HClO_4$. The Bi-PbO_2 electrode was also deposited from a 1 M in $HClO_4$ solution containing 1 mM $Pb(NO_3)_2$ and 0.5 mM $Bi(NO_3)_2$ [24,28].

The *in-situ* spectroelectrochemical experiments were performed in a two-compartment cell, in which the counter electrode was separated from the working and reference electrodes. A bifurcated optical fiber probe was arranged to face a mirror, which was under the transparent bottom of the cell. A platinum foil with its area of about 86 cm^2, which had a semi-cylindrical shape with approximately 1500 holes of about 0.4 mm diameter, surrounded the optical fiber probe as a working electrode above the mirror. The reference electrode was an Ag/AgCl, KCl (sat'd) electrode. A spiral platinum wire was used as the counter electrode. An EG&G

Princeton Applied Research model 173 potentiostat and 175 universal programmer were used for electrochemical experiments. An ORIEL's xenon lamp operating at about 210 w was used as a light source for the spectroscopic measurements. A large electrode area-to-solution volume ratio of about 0.52 cm^{-1} was used to produce a significant amount of products for easier spectroelectrochemical measurements. The optical signal was detected by a charge coupled device (CCD) photon detector, which was interfaced to a 386 computer. The maximum data acquisition rate was 40 spectra per second for the entire spectral range. Nitrogen was purged through the solution to mix the electrolysis solution rapidly and obtain a uniform concentration during the spectroscopic recordings. The details for the setup have been described elsewhere [29,30].

3. Results and Discussion

A series of spectra were recorded during the potential scan in a 10 mM Mn(II) solution. From these spectra, only those at 1.35 V, 1.50 V, and 1.65 V are shwon in *Fig. 1*. A broad peak observed at 475 nm (*Fig. 1 (a)* and *(b)*) is assigned to Mn(III) from the comparison of these spectra with that obtained from the authentic Mn(III) solution [7-10]. We conclude therefore that Mn(III) is produced in this potential range below about 1.5 V. A deep colored film was also seen to be formed on the electrode surface at almost the same time when the Mn(III) is detected. MnO_2 films were reported to be formed under the similar experimental conditions used here [13-19], although the film may contain lower valence ions or oxides under certain experimental conditions [14,15,19]. The spectrum recorded at 1.65 V (*Fig. 1 (c)*) shows the characteristics of MnO_4^-. It is clearly shown from these experiments that when the potential is scanned in a positive direction, both Mn(III) and Mn(IV) are produced first and then both Mn(III) and Mn(VII) are formed in the intermediate potential region,

which is followed by the production of MnO_4^- at higher potentials.
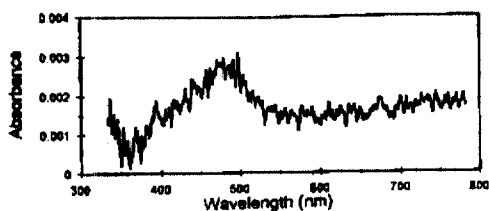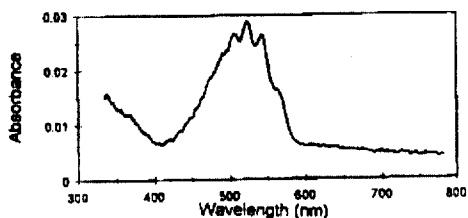

(a)
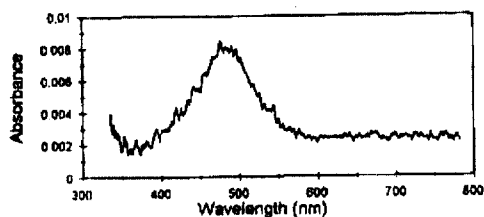
(b)

Fig. 1. *Spectra obtained at 2.35, 1.50, and 1.65 V while scanning the potential.*

Various experimental parameters are shown to exert significant effects on the intermediate and final products of the Mn(II) oxidation. These experimental parameters include: the initial potentials before potential scans, the potentials, the concentration of Mn(II), and the scan rate. Effects of these parameters on the oxidation products at Pt, PbO_2, and Bi-PbO_2 electrodes are summarized in *Table 1*. The effects may be summarized as: high concentrations of Mn(II), slow scan rates, and less positive initial potentials favor the production of

Mn(III), while MnO_4^- is produced under the converse experimental conditions.

The observations described above are explained by the oxidation of Mn(II) to Mn(III) by MnO_4^- according to

$$4Mn(II) + MnO_4^- + 8H^+ \circledR 5Mn(III) + 4H_2O. \qquad [1]$$

As a result, mainly Mn(III) is produced at higher Mn(II) concentrations and slower potential scan rates. At a lower Mn(II) concentration, the rate of reaction [1] is not fast enough to build up Mn(III) rapidly.

We also noticed that the MnO_2 film is formed during the potential scan and the film shows a blocking effect on the formation of MnO_4^-. The spectra (not shown) recorded during the potential at a 20 s interval at a MnO_2 covered Pt, PbO_2, or Bi-PbO_2 electrode exhibited no trace of MnO_4^-. The film is formed only after the potential becomes more positive than 1.6 V in 1 mM Mn(II) solutions. In solutions of higher Mn(II) concentrations, the film was formed at lower potentials.

Results summarized in *Table 1* shows that the MnO_4^- is, in general, more easily produced at PbO_2 or Bi-PbO_2 electrodes than at platinum electrodes in the 10 mM solution. The PbO_2 electrode is regarded as an electrocatalyst, as the electrode itself is a strong oxidant in its +5 oxidation state. However, Randle and Kuhn [12] reported that PbO_2 functions only as a simple inert electrode in sulfuric acid solutions during the oxidation of Mn(II) to Mn(III). Also, bismuth in the Bi-PbO_2 electrodes has been suggested as being an electrocatalyst in its Bi(V) state [34]. The Bi(V) species is a stronger oxidant than PbO_2 [31,32].

A typical current efficiency for the electrochemical generation of Mn(III) and MnO_4^-, as monitored by respective absorbencies, during the potential scan is shown in *Fig. 2* along with linear sweep voltammograms recorded simultaneously. These experiments revealed that the permanganate is effectivley produced at the Bi-PbO_2 electrode. Also, it can be seen from this figure that

Table 1. Major Oxidation Products under Different Experimental Conditions

Electrodes	Pt		PbO$_2$	Bi-PbO$_2$	
Scan range, V vs. Ag/AgCl	1.2 - 1.8	1.5 - 1.8	1.5 - 1.8	1.2 - 1.8	1.5 - 1.8
1 mM, 1 mV/s	MnO$_4^-$	MnO$_4^-$	MnO$_4^-$	MnO$_4^-$	MnO$_4^-$
10 mM, 1 mV/s	Mn(III)	Mn(III)	Mn(III)/MnO$_4^-$	Mn(III)	Mn(III)/MnO$_4^-$
100 mM, 1 mV/s	Mn(III)	Mn(III)	Mn(III)	Mn(III)	Mn(III)
10 mM, 10 mV/s	Mn(III)/MnO$_4^-$	--^{b}	--^{b}	Mn(III)/MnO$_4^-$	--^{b}

Mn(III) is produced as an intermediate species en route to the formation of permanganate ion.
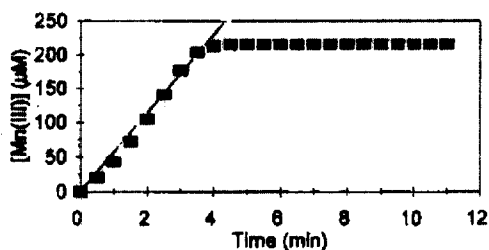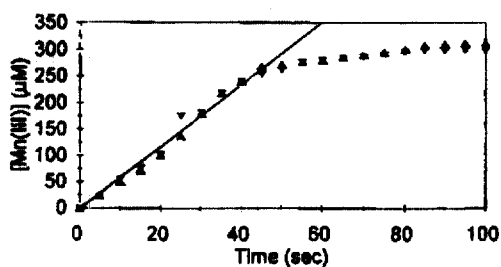

Fig. 2. Linear sweep voltammogram (top) along with absorbances (bottom) recorded at 475 nm (1) and 525 nm (2).
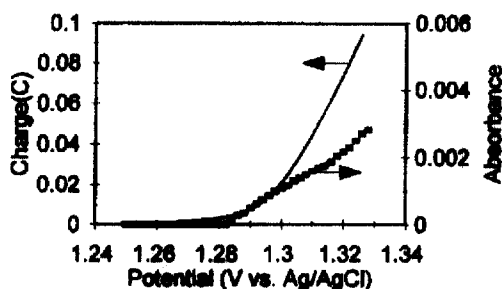

Fig. 3. The electrolysis charge and absorbance plotted as a function of potential during the potential scan at a scan rate of 1 mV/s.

Shown in *Fig. 3* are the charge (solid line) and corresponding absorbance observed (dotted squares) during the voltammetrics canning *vs.* potential plots at the stationary platinum electrode. One can see in the figure that the rise in absorbance is similar to that in charge below about 1.29 V, slows down significantly in the intermediate region, and becomes somewhat faster above about 1.32 V. This behavior may result from the equilibrium reaction between the products formed at the electrode surface.

When the thermodynamics of the reactions involved is considered, the oxidation of Mn(II) should produce MnO_2 first and then Mn(III) at less positive potentials. The standard electrode potential, E^0, for the MnO_2/Mn^{2+} couple is 1.23 V vs. NHE, whereas it is 1.5 V for the Mn(III)/Mn^{2+} [31]. However, our results show that soluble Mn(III) appears to be produced before the formation of the MnO_2 film. We believe that the E^0 values reported in the literature may have a large margin of error. From this observation, we conclude that the initial step for the Mn(II) oxidation should be the generation of a soluble Mn(III) species. The MnO_2 film is then formed by the disproportionation reaction of the Mn(III) species, or by forming a MnOOH layer followed by a further oxidation to MnO_2 [14-19]. The MnO_2 thus formed may produce Mn(III) back by the conproportionation reaction,

$$2Mn(III) + 2H_2O \_ MnO_2 + Mn(II) + 4H^+ \qquad [2]$$

4. Conclusions

The electrochemical oxidation of Mn(II) is affected significantly by various experimental parameters. More positive potentials, low concentrations of Mn(II), faster scan rates, and more positive initial potentials favor the formation of MnO_4^-, while the converse favors the production of Mn(III). These observations are explained by the blocking effect of the MnO_2 film and the respective stabilities of the electrogenerated products under different conditions. The PbO_2 and Bi-PbO_2 electrodes show catalytic activities for the oxidation of Mn(II) to MnO_4^-, but not for the oxidation of Mn(II) to Mn(III). The soluble Mn(III) species is formed at less positive potentials during the oxidation, followed by the equilibrium reaction, reaction [2], in either direction depending on the concentration of each species at more positive potentials.

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