Reinvestigation of the Electrochemical Reduction of $KMnO_4$

San-Chung LIN, Yung-Yun WANG,* Chi-Chao WAN, and J. -Cheng CHANG†
Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.
†Chung Shan Institute of Science and Technology, Lungtan, Taiwan, R.O.C.

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Investigating the electrochemical reduction behavior of MnO_4^-, we determined the consecutive reduction/oxidation potentials of MnO_4^- by the cyclic voltammetric method. We have also confirmed that MnO_4^{2-} is reduced into MnO_4^{3-}. We then investigated the cause of the generation of MnO_2 on the electrode surface with the rotating ring-disk electrode method. The reversibility of the reduction of MnO_4^- depends on the concentration of $KMnO_4$ and KOH. Reversibility increases when the concentration of KOH increases, but the reversibility decreases when the concentration of $KMnO_4$ increases. The reaction rate of MnO_4^-/MnO_4^{2-} follows the law:

$$\text{reaction rate} = kC_{\text{KMnO}_4}^{0.4}C_{\text{KOH}}.$$

$KMnO_4$ is a well-known oxidizing agent used in many applications.[1,2] $KMnO_4$ has also been used in the desmearing step during the process of manufacturing PCB.[3—5] Because the oxidation capability is decreased with the consumption of $KMnO_4$, an electrochemical regeneration is needed to maintain the $KMnO_4$ concentration. Thus understanding the electrochemical behavior of $KMnO_4$ is important.

There have been several studies of the kinetics and reversibility of the reduction/oxidation of $KMnO_4$;[6—15] however, many results differ significantly. For example, Plieth[16] suggested that there is an adsorption step and partial charge transfer in the reduction/oxidation of MnO_4^-/MnO_4^{2-}, whereas Freeman[17] believed the reaction to be a single electron transfer and to lack an adsorption step.

We present here results of a systematic study, by means of cyclic voltammetry (CV), a rotating ring-disk electrode (RRDE), linear sweep voltammetric (LSV) method etc., of the electrochemical reduction of $KMnO_4$ on the platinum electrode. The results are expected to help us understand better and to improve the design and operation of the $KMnO_4$ electrolytic regeneration system.

Experimental

1) Cyclic Voltammetric (CV) Analysis. A solution (500 ml) of $KMnO_4$ (10^{-3} M, M=mol dm^{-3}) and KOH (2 M) was prepared and placed in an electrolysis cell. The working electrode was a platinum disk electrode having a surface area 0.164 cm^2. The counter electrode was a 3.2×3.9×0.05 cm platinum plate and the reference electrode was a saturated calomel electrode (SCE). The relationship of potential and current was recorded with an X–Y recorder. The range of scan potential was between 0.45 and −0.22 V (vs. SCE) and the scan rate was 200 mV s^{-1}.

Three reduction peaks (I, II, III) and two oxidation peaks (IV, V) were discovered. Subsequently several methods were used to identify the resulting product after electrolysis under constant potential.

2) Rotating Ring-Disk Electrode (RRDE) Analysis. A solution (500 ml) of $KMnO_4$ (10^{-3} M) and KOH (1 M) was prepared and placed in the electrolysis cell. The working electrode was an RRDE. The diameters of the outer ring, inner ring and disk are 0.538, 0.492, and 0.457 cm, respectively. The RRDE was rotated at 200 rpm. The ring electrode potential was set at 0.4 V (vs. SCE) and the disk electrode potential was scanned from 0.4 to −0.1 V (vs. SCE) at 1 mV s^{-1} scan rate.

3) Linear Sweep Voltammetric (LSV) Analysis. Solutions (500 ml) of various concentrations containing $KMnO_4$ (5×10^{-4}—10^{-2} M) and KOH (0.1—2 M) were prepared. The relationship between the peak potential and the concentration of $KMnO_4$ and KOH was plotted.

Results and Discussion

1) Electrochemical Reduction Behavior of MnO_4^-.

The standard electrode potentials of MnO_4^- reduction reaction are expressed as follows:[18]

$$MnO_4^- + e \longrightarrow MnO_4^{2-} \quad E^0 = 0.57 \text{ V (vs. SHE)} \quad (1)$$

$$MnO_4^- + 2e \longrightarrow MnO_4^{3-} \quad E^0 = 0.42 \text{ V (vs. SHE)} \quad (2)$$

$$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^- \quad E^0 = 0.59 \text{ V (vs. SHE)} \quad (3)$$

The CV results of $KMnO_4$/KOH solution are shown in Fig. 1. The curve indicates that there are three reduction peaks (I, II, III) and two oxidation peaks (IV, V). The reduction peak potentials are 0.31, 0.01, and −0.19 V (vs. SCE), whereas oxidation peaks occur at 0.35 and 0.1 V. Peaks I (II) and V (IV) are the corresponding reduction/oxidation reaction, but peak III has no corresponding oxidation reaction.

When the solution was electrolyzed at 0.31 V for two hours, the color changed from purple to green without any formation of deposit on the electrode. When Ba^{2+} was added to the solution, a green deposit was formed. Thus we conclude that the reaction product was $BaMnO_4$.[7] Therefore single electron transfer took place and MnO_4^- was reduced to MnO_4^{2-}.

When the solution was electrolyzed at 0.01 V, a brown deposit was formed on the platinum electrode.

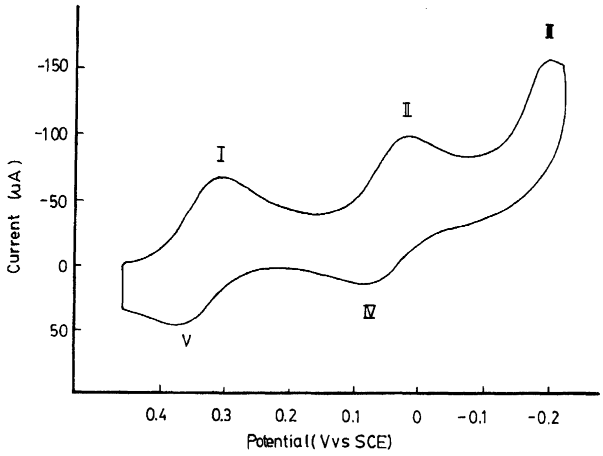

Fig. 1. CV diagram of $KMnO_4$/KOH solution.

The deposit was analyzed with AA spectrometry and a titration method and was confirmed to be MnO_2. The result is consistent with Desideri's report.[7] However, Schuring,[11] Brzezinska,[12] and Freeman[17] suggested that the reaction occurring at this potential should be reduction of MnO_4^{2-} to MnO_4^{3-}.

A special potential scanning technique[19] was used to elucidate the number of electrons transferred during a reaction having multiple consecutive steps. In our experimental system, the potential was scanned from 0.43 to 0.2 V at a rate 200 $mV\,s^{-1}$, then the electrolysis was conducted under 0.2 V until the current reached a steady state. Finally the potential was scanned from 0.2 V to −0.1 V at 200 $mV\,s^{-1}$. The current–potential relation is shown in Fig. 2. Two current peaks were observed at 0.3 and 0 V. The peak current is expressed according to the Randles–Sevcik equation:[20,21]

$$i_{p1} = 0.4463 n_1 FA(n_1F/RT)^{1/2} D_1^{1/2} \nu^{1/2} C_1^* \quad (4)$$

$$i_{p2} = (n_1 + n_2) i_{ss} + 0.4463 n_2 FA(n_2F/RT)^{1/2} D_2^{1/2} \nu^{1/2} C_2^* \quad (5)$$

in which n_1 and n_2 are the numbers of electrons transferred during the first and second steps of reaction, n_1 is equal to one. D_1 and D_2 are the diffusion coefficients of the first and second steps of reaction. The values of D_1 and D_2 (D_1/D_2=$4.57\times10^{-10}/3.45\times10^{-10}$) are obtained from Landsberg.[10]

Combining Eqs. 4 and 5, we obtain

$$i_{p1}/[i_{p2} - (n_1 + n_2) i_{ss}] = (n_1/n_2)^{3/2} (D_1/D_2)^{1/2} \quad (6)$$

With the data shown in Fig. 2, we find $n_2 \approx 1.1$. The result means that the number of electrons transferred in the second step of reaction is approximately one. Thus we believe that the reaction which occurred at 0.01 V is the reduction of MnO_4^{2-} to MnO_4^{3-}. This conclusion seems to agree with the suggestion of Freeman et al.

As an MnO_2 deposit was formed simultaneously, we believe that part of MnO_4^{3-} can become MnO_2 through a chemical reaction proposed by Ladbury.[22]

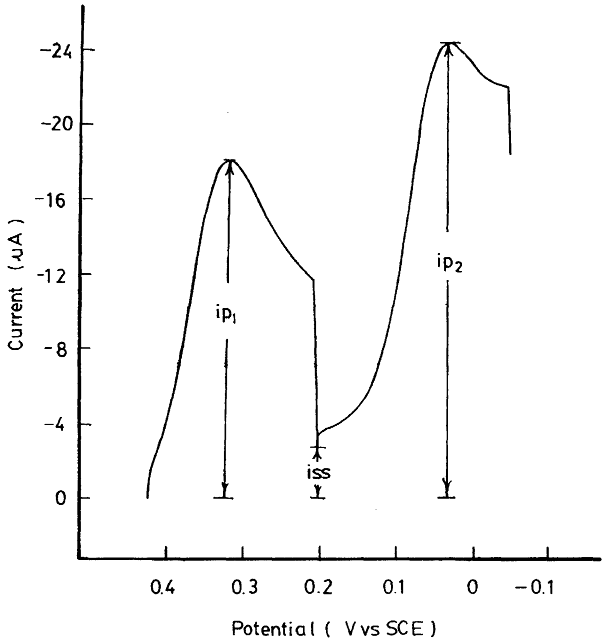

Fig. 2. Relationship between current and scanning potential of $KMnO_4$/KOH solution.

$$2MnO_4^{3-}(aq) + 2H_2O \longrightarrow MnO_2(s) + MnO_4^{2-}(aq) + 4OH^-(aq) \quad (7)$$

Further studies were conducted to confirm this hypothesis. When the solution was electrolyzed at −0.19 V for five hours, we found a black substance generated on the surface of the platinum electrode. The analysis results showed that this material was also MnO_2. However, the brown MnO_2 had good adhesion to the platinum electrode while the black MnO_2 did not. The reason is probably that the latter is the result of electrochemical reduction of MnO_4^{3-} to MnO_2.

Figures 3 and 4 illustrate the disk current i_d and the ring current i_r of the RRDE, respectively. From the definition of the collection factor N,[23]

$$N = -i_r/i_d \quad (8)$$

and by measuring i_{d_1} and i_{r_1} from the limiting currents shown in Figs. 3 and 4, we computed that N_1 of the MnO_4^-/MnO_4^{2-} reaction is 0.218, which is very close to the theoretical value of 0.221. From the peak currents i_{d_2} and i_{r_2}, we calculated that N_2 of the $MnO_4^-/MnO_4^{2-}/MnO_4^{3-}$ reaction is 0.210. The value of N_2 is slightly smaller than that of N_1, although in theory they should be identical. The reason is that as MnO_4^{2-} is reduced to MnO_4^{3-}, a portion of the latter forms MnO_2. Consequently, the amount of MnO_4^{3-} moving toward the ring electrode decreases, and the value of the collection factor also decreases.

2) Reversibility of the MnO_4^-/MnO_4^{2-} Couple. Figure 5 shows the CV diagram of a solution containing $KMnO_4$ (5×10^{-4} M) and KOH (2 M). The reduction current shown is the result of the reduction

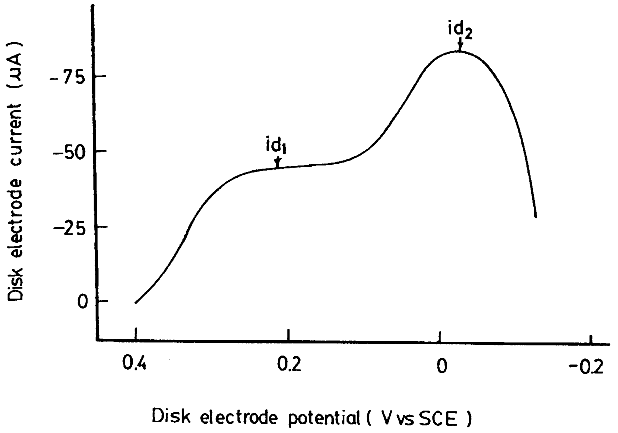

Fig. 3. Relationship between disk electrode current and disk electrode potential of KMnO4/KOH solution.

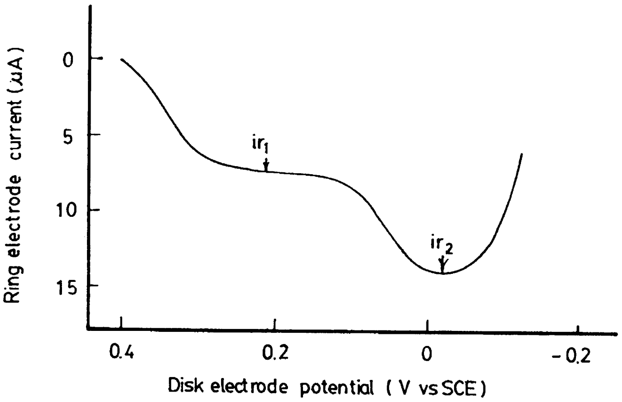

Fig. 4. Relationship between ring electrode current and disk electrode potential of KMnO4/KOH solution.

of MnO_4^- to MnO_4^{2-}, the corresponding oxidation current is the reverse oxidation reaction. Nicholson[24] suggested a correlation between peak potential difference ΔE_p and the φ function, and Matsuda[25] used the coefficient of the reaction rate to classify the reversibility. Based upon the combination of these two criteria, we found that when ΔE_p was smaller than 62 mV, the reaction is considered reversible. Meanwhile, when ΔE_p exceeded 62 mV, the reaction approached quasi-reversible. This method, although providing the same conclusion as those proposed by Greef,[26] is considerably simpler. Obviously the above reaction couple is close to reversible. Figure 6 shows the CV diagram of a solution of $KMnO_4$ (10^{-2} M) and KOH (0.1 M). Similarly, we conclude that this system is quasi-reversible as the rate constant can be computed to be 10 cm s^{-1} based on CV data.

From the experiments described above, we found that the reversibility of the system depended on the concentrations of $KMnO_4$ and KOH. Probably for this reason the reversibility of MnO_4^-/MnO_4^{2-} reaction has been found to be either reversible, irreversible or quasi-reversible in different studies.[7,11,13] Table 1 summarizes ΔE_p values of various $KMnO_4$/KOH solutions. The results show that with a constant concentration of KOH, ΔE_p increases if the concentration of $KMnO_4$ increases; consequently, the reversibility decreases. In contrast if

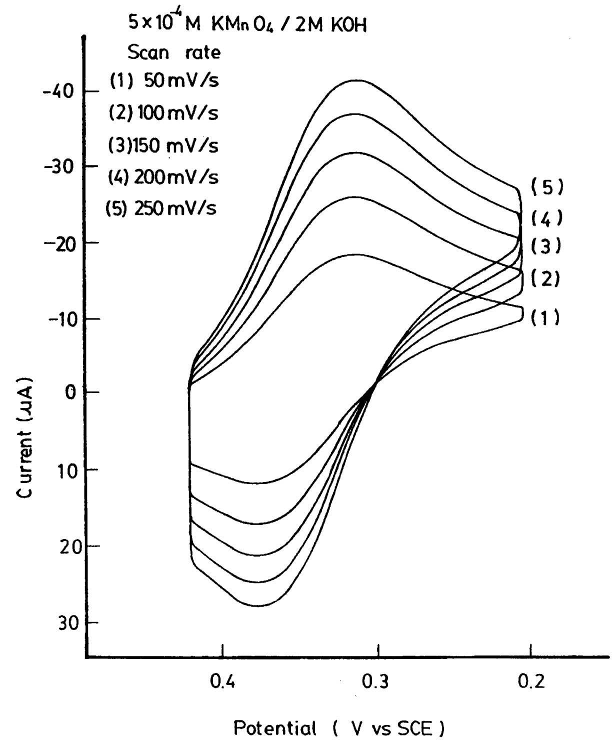

Fig. 5. CV diagram of $KMnO_4$ (5×10^{-4} M)/KOH (2 M) solution.

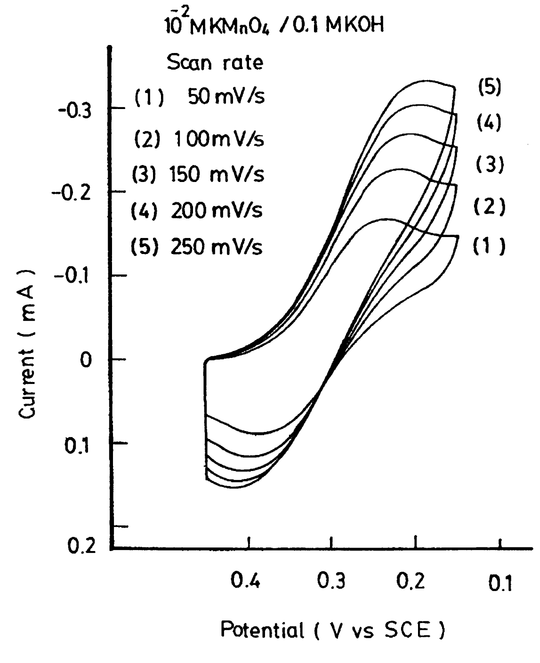

Fig. 6. CV diagram of $KMnO_4$ (10^{-2} M)/KOH (0.1 M) solution.

one fixes the concentration of $KMnO_4$, ΔE_p decreases as the concentration of KOH increases, and the reversibility increases.

With the same diagnosis criteria, we found that the reaction of MnO_4^{2-}/MnO_4^{3-} is between reversible and quasi-reversible, and MnO_4^{3-}/MnO_2 is irreversible. The results agree with those of previous reports.[11,12,17]

3) Reaction Rate of the MnO_4^-/MnO_4^{2-} Couple. Parker[27] showed how to obtain a rate equation by means of the linear sweep voltammetric method. A reaction rate is expressed as follows:

$$\text{rate} = k_{\text{obs}} C_a^a C_b^b C_i^i C_x^x \tag{9}$$

$$\partial E_p / \partial \log (C_a) = -[(a+b+i+x-1)/(b+1)]RT/nF \tag{10}$$

$$\partial E_p / \partial \log (C_x) = [x/(b+1)]RT/nF \tag{11}$$

in which

k_{obs} : reaction rate coefficient
C_a : reactant concentration
C_b : product concentration
C_i : intermediate concentration
C_x : supporting electrolyte concentration

From our experiments, we found that the reaction rate is a function of the concentrations of reactant and supporting electrolyte. One possible explanation for the dependence on the KOH concentration is that MnO_4^- is not entirely stable in the KOH solution and may gradually be reduced to MnO_4^{2-} chemically. Thus when we assume b=0 and i=0 in Eq. 9, the reaction rate becomes rewritten as:

$$\text{rate} = k_{\text{obs}} C_{\text{KMnO}_4}^a C_{\text{KOH}}^x \tag{12}$$

$$\partial E_p / \partial \log C_{\text{KMnO}_4} = -(a+x-1)RT/nF \tag{13}$$

$$\partial E_p / \partial \log C_{\text{KOH}} = xRT/nF \tag{14}$$

Figure 7 is a plot of the value of E_p as a function of the logarithm of the concentration of KOH. The slope is about 26 mV/dec. and the value of x is about 1. Similarly, we found that a is approximately equal to 0.4 from the value of the slope in Fig. 8. Substituting these values back to Eq. 12, we express the reaction rate of MnO_4^-/MnO_4^{2-} as

$$\text{rate} = k_{\text{obs}} C_{\text{KMnO}_4}^{0.4} C_{\text{KOH}} \tag{15}$$

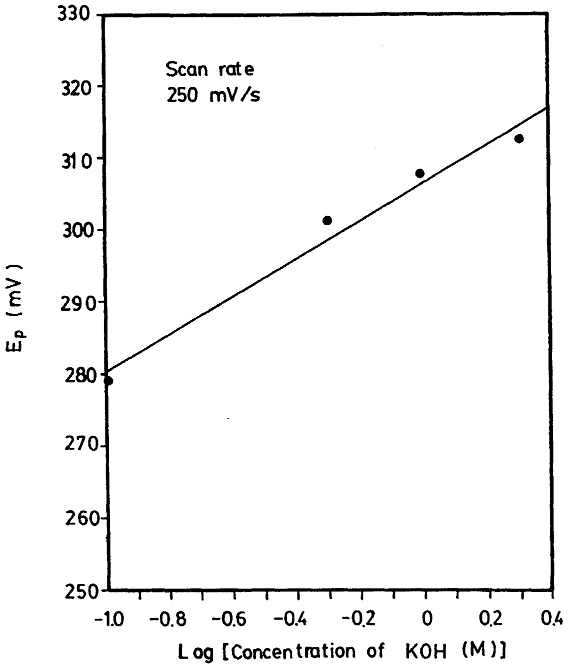

Fig. 7. Relationship between E_p and concentration of KOH.

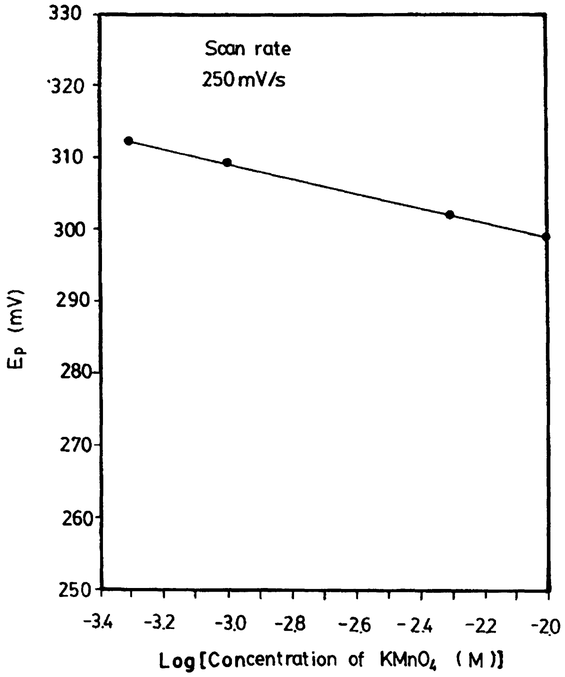

Fig. 8. Relationship between E_p and concentration of $KMnO_4$.

Conclusion

We have investigated the electrochemical behavior of $KMnO_4$ systematically. We found that $KMnO_4$ is first reduced to MnO_4^{2-}, and then continuously reduced to MnO_4^{3-} and MnO_2. We also found that the observed brown deposit of MnO_2 on the platinum electrode is produced via a hydrolysis reaction of MnO_4^{3-}.

Table 1. Values of ΔE_p/mV of Various $KMnO_4$/KOH Solutions at Scan Rate 50 mV s^{-1}

$KMnO_4$/M	10^{-2}	10^{-3}	5×10^{-4}
KOH/M			
0.1	151	100.7	99.8
1.0	95.8	77.4	72.8
2.0	79.2	65.8	62.8

We propose that the reversibility of reduction/oxidation of MnO_4^-/MnO_4^{2-} is dependent on the concentrations of $KMnO_4$ and KOH. When the concentration of KOH increases, the reaction rate increases, and the reversibility increases. Conversely the reversibility decreases as the concentration of $KMnO_4$ increases. We also found that MnO_4^{2-}/MnO_4^{3-} is between reversible and quasi-reversible, and that MnO_4^{3-}/MnO_2 is irreversible.

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