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# Comparison of the Oxygen Reduction Reaction between NaOH and KOH Solutions on a Pt Electrode: The Electrolyte-Dependent Effect

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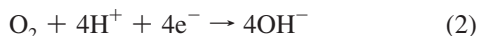
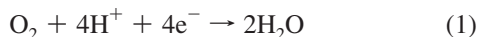
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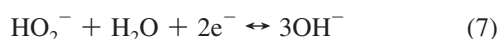
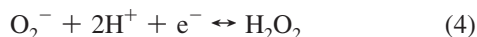
The oxygen reduction reaction (ORR) on a polycrystalline Pt surface was studied using cyclic voltammetry techniques, and the influence of reaction media on the ORR is examined by comparing the ORR in NaOH and KOH solutions with concentration ranging from 0.5 to 14 M at 298 K. The results show that, in NaOH and KOH solutions, the ORR, a quasi-reversible diffusion-controlled reaction, is largely dependent on the electrolyte conditions, and KOH solutions are superior to NaOH solutions for the ORR process in both thermodynamic and kinetic consideration. As the alkaline concentration increases, the ORR performance frustrates, and the protonation of superoxide is suppressed; thus, the ORR shifts from a 2e reduction pathway to a 1e reduction pathway in both solutions.

## 1. Introduction

Due to the widespread application in fuel cell technology, corrosion engineering, biology process, and some other important fields,<sup>1,2</sup> the oxygen reduction reaction (ORR) continues to attract considerable research attention. Previous studies have suggested that, depending on the electrode and electrolyte involved, the ORR could happen via two schemes,<sup>3</sup> which are “direct” 4e reduction and “series” 4e reduction. The “direct” 4e reduction scheme is characterized by the one-step reduction of oxygen to water in acidic media or hydroxyl ion in basic media, as shown in eqs 1 and 2, respectively.<sup>4</sup>



In contrast, during the “series” 4e reduction process, oxygen is first reduced to superoxide anion, as seen in eq 3,<sup>5</sup> followed by further reduction to hydrogen peroxide molecule as the intermediate and water as the final product<sup>6</sup> (eqs 4 and 5, respectively) in acidic media and to hydrogen peroxide anion as the intermediate and hydroxyl ion as the final product (eqs 6 and 7, respectively) in basic solutions.<sup>7,8</sup>



For example, using Pt and Ag electrodes, the ORR mainly proceeds via 4e reduction,<sup>9,10</sup> while, on a Au electrode, the 2e

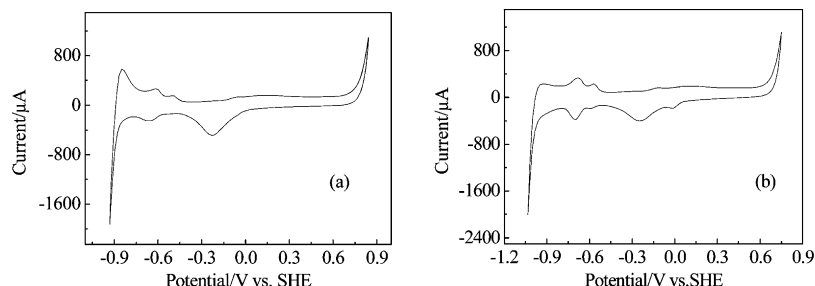
reduction to  $\text{H}_2\text{O}_2$  is the dominating reaction in acidic solutions independent of surface structure,<sup>11</sup> but the 4e reduction occurs on Au(100) in alkaline solutions.<sup>12</sup> Besides, superoxide is identified to be the reaction product of the ORR in aprotic solutions<sup>13,14</sup> and the intermediate of the “series” pathway in aqueous solutions.<sup>6</sup> Due to the disproportionation of  $\text{O}_2^-$  and rapid protonation induced by  $\text{H}^+$  or  $\text{H}_2\text{O}$ ,<sup>15,16</sup> the lifetime of  $\text{O}_2^-$  in most aqueous solutions is significantly short and thus the initial step of ORR represents apparent 2e reduction to  $\text{H}_2\text{O}_2$  or  $\text{HO}_2^-$ .<sup>17</sup> However, similar to aprotic solutions, the strong alkaline concentration can promote the existence of  $\text{O}_2^-$ , as suggested from reaction 7.<sup>18</sup>

It is obvious that the “direct” and “series” pathways of the ORR are electrolyte dependent and both the thermodynamics and the kinetics of the ORR can be manipulated by adjusting the reaction media. The influence of electrolyte on the electrochemical reaction kinetics has been studied extensively with respect to the acceptor number of solvent,<sup>19</sup> solvent molecule size,<sup>20</sup> corresponding dielectric constants with concentrations,<sup>21</sup> and solvation energies of oxidant and reductant.<sup>22</sup> Further, electrochemical kinetics is substantially affected by the viscosity of electrolyte. The diffusion coefficient of reactant varies with the solution viscosity,  $\eta$ , as predicted by the Stokes–Einstein equation,<sup>23</sup> while Zhang<sup>24</sup> discovered the dependence of rate constants of heterogeneous electron transfer reactions on viscosity. As compared to other solvent effects in other electrochemical systems, the ORR kinetics is closely related to the electrolyte-dependent oxygen behavior. Reeve<sup>25</sup> observed the effect of the minority additives to various molten alkali carbonate electrolytes for ORR kinetics, which originated from the increasing oxygen solubility,  $\text{CO}_2$  diffusion, and meniscus effects. Floriano<sup>26</sup> attributed the ORR on the platinum/proton exchange membrane interface to the electrolyte concentration, oxygen solubility, and diffusion coefficient. Zhang et al.<sup>27</sup> investigated the ORR on Pt in NaOH solutions of different concentrations and identified that the decreasing charge density stems from the decreasing oxygen solubility and diffusion coefficient, while the diffusion coefficient was linear with viscosity.

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**Figure 1.** CV curves of a polycrystalline Pt wire electrode (diameter, 0.75 mm) in Ar saturated (a) 0.5 M and (b) 8 M NaOH solution at 298 K, respectively. Scan rate: 100 mV/s.

Besides the oxygen behavior, the anion adsorption also plays a significant role in the electrolyte-dependent effect for electroreduction of oxygen. Considerable research has been carried out on the solvent anion adsorption on an electrode such as bisulfate, hydroxyl, and halides, revealing the adverse electrochemical effects.<sup>28,29</sup> In the presence of strongly adsorbed anions, the ORR suffers further overpotential losses, and the ORR activity decline is consistent with the increase of bond strength and surface coverage.<sup>30</sup> Hsueh<sup>31</sup> studied the ORR process on Pt in several solvents and assumed the solvent effect arises from the surface coverage of anion adsorption of media from the competition for the adsorbed sites with other reactive intermediates. Consequently, on the basis of investigations of the structure-sensitive ORR process,<sup>32</sup> together with the facilitating impact of the ORR in the presence of  $\text{Cl}^-$  or by using the Pt alloy (mostly with transition metals as Co, Ni, Cr, and Fe) electrodes,<sup>33,34</sup> it has long been recognized that the PtOH formation inhibits the oxygen reduction.<sup>35</sup> In alkaline media,  $\text{OH}_{\text{ads}}$  is not only a spectator species blocked by the surface but also the important intermediate of the ORR which is assumed to have an energetic effect on the kinetics of oxygen reduction, through the change of Gibbs energy.<sup>36</sup>

Sodium hydroxide and potassium hydroxide are the most important alkaline electrolytes for the electro-reduction of oxygen.<sup>37</sup> Due to the size difference between potassium and sodium cations, many of the physicochemical properties such as solution viscosity,<sup>38</sup> oxygen solubility,<sup>39,40</sup> oxygen diffusion coefficient,<sup>40,41</sup> electrode interfacial phenomena,<sup>42</sup> etc., are quite different. Therefore, the electrochemical behavior of the ORR in these two electrolytes is expected to be different. However, although many efforts have been made to understand the ORR behavior in NaOH and KOH separately, the comparison of ORR activity in these electrolytes, especially in the concentrated solutions, is scarce. In this regard, the aim of this study is to investigate the ORR behavior in NaOH and KOH solutions by cyclic voltammetry (CV) in order to compare the ORR behavior and provide further information regarding the mechanisms of the electrolyte-dependent effect of the ORR in alkaline solutions.

## 2. Experimental Section

A series of NaOH and KOH aqueous solutions with concentrations ranging from 0.5 to 14 M were prepared by dissolving NaOH and KOH pellets (both p.a. grade, Merck) in the high purity Milli-Q water. Alkaline solutions, saturated with highly pure Ar and  $\text{O}_2$  (99.998 and 99.999% by volume, respectively, Beijing Jingchen Gas), were employed as the blank and working solution, respectively.

Experiments were conducted in a thermostatic standard three-compartment electrochemical cell at  $298 \pm 0.2$  K by using an electrochemical workstation (IM6e, ZAHNER). The working electrode was a polycrystalline Pt (99.999% purity) cylinder

electrode, 0.75 mm in diameter, embedded in borosilicate glass. It possesses an effective area of  $0.711 \text{ cm}^2$ . A large-area Pt foil was used as the counter electrode, and the reference electrode was a  $\text{HgO}/\text{Hg}$  (14 M NaOH, 0.006 V vs SHE) electrode, sealed within a Luggin capillary. The etching effect on the glass caused by strongly alkaline solutions was confirmed to be minimal.

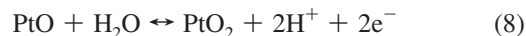
Prior to each measurement, the Pt cylinder and Pt foil electrodes were washed with ethanol in an ultrasonic cleaner, and polished with a  $0.3 \mu\text{m}$  alumina–water suspension. Then, the electrodes were repeatedly rinsed and cleaned with ethanol and water in the ultrasonic cleaner to obtain a contamination free electrode surface. After that, electrodes were cycled in Ar or  $\text{O}_2$  saturated solutions between the onset potential of  $\text{H}_2$  and  $\text{O}_2$  evolution reactions until reproducible cyclic voltammetry curves were obtained, while the final potential was stopped at the onset of  $\text{H}_2$  evolution. All of the potentials presented are versus the standard hydrogen electrode (SHE).

The solution viscosity was measured with an Ubblohe type suspended level capillary viscometer (NDJ-5S with capillary 0c and 15–20 mL capacity, Shanghai Sunny Hengping). The viscometer filled with NaOH or KOH solution was placed vertically in a continuously stirred water bath at  $298 \pm 0.2$  K (DHX-05 type, Ningbo Dongsheng), and the viscosity was automatically measured. The accuracy approached up to 0.02% in the dilute region and 0.05% in the concentrated region.

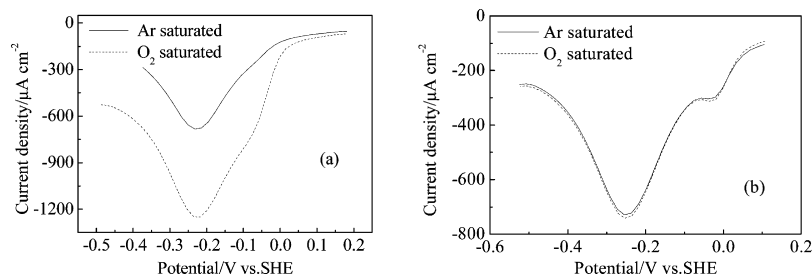
## 3. Results and Discussion

**3.1. Electrochemical Reactions at the Pt Surface.** Figure 1 shows the typical CV curves of a polycrystalline Pt electrode in Ar saturated 0.5 and 8 M NaOH solutions at a scan rate of 100 mV/s, respectively. From the CV curve in Ar saturated 0.5 M solution, the  $\text{H}_2$  evolution peak is observed at  $-0.9$  V, and the so-called “butterfly region” ( $-0.67 \text{ V} < E < -0.42 \text{ V}$ ) is due to the highly reversible adsorbed hydroxyl. The formation of irreversible platinum oxide occurs at  $-0.07$  V, and its reduction peak emerges at  $-0.23$  V. All of these peaks are consistent with previous investigations in alkaline solutions.<sup>43</sup>

Besides, in 8 M Ar-saturated solution, similar to the CV curves observed in 0.5 M NaOH solution, the  $\text{H}_2$  evolution and Pt electrode surface involved reactions exist. However, it is interesting to notice that a tiny pair of peaks appear at around  $-0.01$  V, which are possibly attributed to the further oxidation/reduction of the Pt surface to generate  $\text{PtO}_2$  as expressed in eq 8<sup>44</sup> according to Bockris et al.



Besides, the peak potential of PtOH formation negatively shifts from  $-0.669$  V in 0.5 M to  $-0.773$  V in 8 M NaOH solution, indicating the PtOH formation reaction is strengthened



**Figure 2.** CV curves of the ORR at a polycrystalline Pt electrode in Ar and O<sub>2</sub> saturated (a) 0.5 M and (b) 8 M NaOH solution at 298 K, respectively. Scan rate: 100 mV/s.

**TABLE 1: Comparison of the ORR Behavior in NaOH and KOH Solutions Ranging from 0.5 to 14 M at 298 K, Scan Rate: 100 mV/s**

concentration (mol·L <sup>-1</sup> )	peak potential of ORR (V)		current density of ORR (μA·cm <sup>-2</sup> )	
	NaOH	KOH	NaOH	KOH
0.5	-0.231	-0.215	592.60	685.13
1	-0.234	-0.219	385.32	492.57
1.5	-0.237	-0.223	218.69	326.55
2	-0.239	-0.225	133.46	208.49
4	-0.243	-0.230	58.31	94.43
6	-0.247	-0.234	26.42	45.91
8	-0.251	-0.239	7.89	11.44
12	-0.262	-0.249	0.58	1.04
14	-0.270	-0.258	0.25	0.63

with electrolyte concentration, which agrees well with previous studies.<sup>45</sup> This electrolyte-dependent surface property and its correlation with the ORR process will be explained in detail later.

The oxygen reduction reactions carried out in 0.5 and 8 M NaOH solutions saturated with Ar and O<sub>2</sub> are illustrated in Figure 2. The oxygen reduction occurred at -0.231 V in 0.5 M O<sub>2</sub> saturated solution, and it has long been recognized that the current density observed at this potential (-0.231 V) is the sum of the oxygen reduction current density, platinum oxide reduction current density, and double-layer charging current density. Therefore, the current density of the ORR was calculated by taking the current density difference in Ar and O<sub>2</sub> saturated solutions. By comparing the CV curves obtained in 0.5 and 8 M solutions, it is clear that, as the solution concentration increases, the ORR current density substantially reduces from 592.6 to 7.89 μA·cm<sup>-2</sup>, and the ORR peak potential negatively shifts from -0.231 to -0.251 V, suggesting the frustration of the ORR due to the increase of alkaline concentrations. Besides, in concentrated alkaline solutions, owing to the very small oxygen solubility and high solution viscosity, the current density of the ORR is small and its determination became difficult. Therefore, it took several repeated measurements to obtain reproducible data, and a similar observation has also been reported previously.<sup>46</sup> The CV curves in other dilute (<8 M) NaOH and KOH solutions are very similar to that observed in 0.5 M NaOH solution, and the curves in other concentrated (>8 M) NaOH and KOH solutions are very similar to that in 8 M NaOH solution.

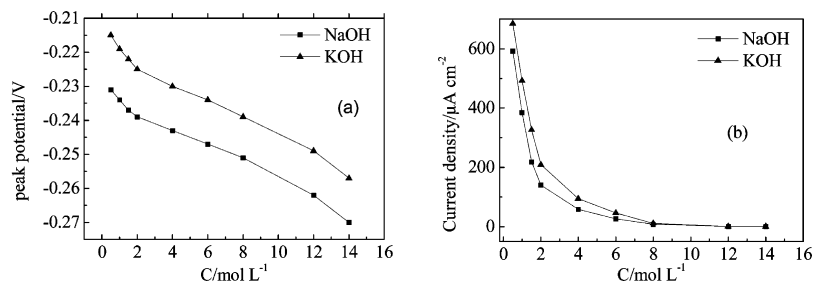
**3.2. Comparison of the ORR in NaOH and KOH Solutions.** The comparison of the ORR behavior in NaOH and KOH solutions is summarized in Table 1, which exhibits values of peak potential and current density of the ORR in alkaline solutions at different concentrations. For better illustration, the dependence of the ORR peak potential and current density on

solution concentration is plotted in Figure 3. It is clearly seen in Table 1 and Figure 3 that, in both NaOH and KOH solutions, as the electrolyte concentration increases, the peak potential negatively shifts monotonically and the current density significantly decreases, indicating the depressing effect of the ORR as the electrolyte concentration increases. Furthermore, the peak potential of the ORR in KOH solutions is clearly more positive than that in the corresponding NaOH solutions, and the current density in KOH solutions is larger than that in the corresponding NaOH solutions, suggesting KOH solution is a superior media for the ORR in both thermodynamic and kinetic considerations in comparison with NaOH solution. The above-mentioned observations are partially due to the electrolyte-concentration-dependent characteristic of the Pt involved surface interactions and partially due to the oxygen transport properties in alkaline solutions, which will be further explained in the following sections.

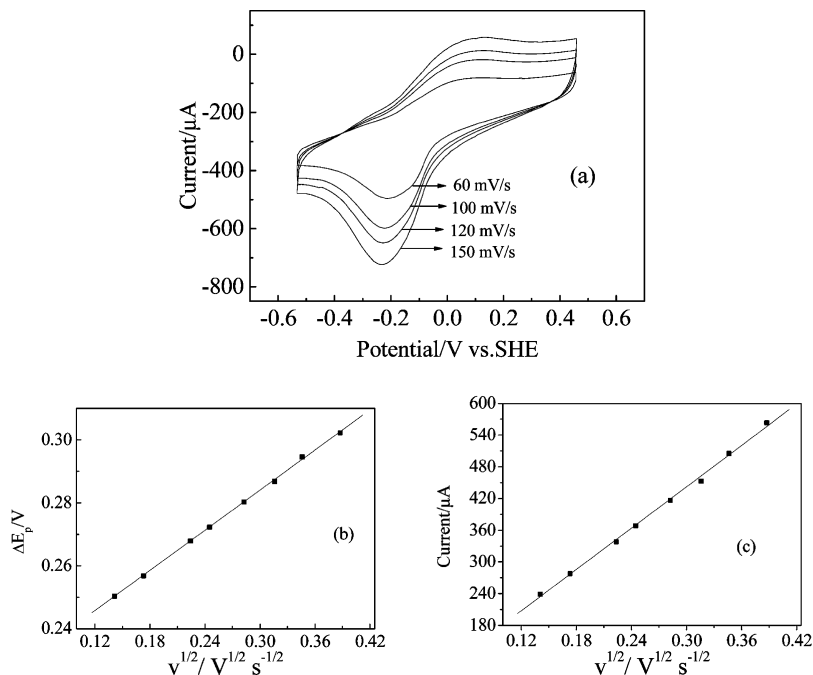
**3.3. Reaction Kinetics and Mechanisms of the ORR in NaOH and KOH Solutions.** In order to determine the reaction kinetics of the ORR in NaOH and KOH solutions, the CV curves of different scan rates (from 20 to 150 mV/s) in oxygen saturated KOH solution were recorded, and are presented in Figure 4a. As can be seen in Figure 4a, the separation between the anodic and cathodic peaks ( $\Delta E_p$ ) is larger than expected for a reversible process and the cathodic peak potential ( $E_{pc}$ ) of the ORR negatively shifts from -0.210 V at 60 mV/s to -0.236 V at 150 mV/s, suggesting the ORR in 1 M KOH is only quasi-reversible. Further,  $\Delta E_p$  of ORR shows a linear relationship with the square root of the scan rate ( $v^{1/2}$ ), as seen in Figure 4b, in good agreement with the theory for a typical quasi-reversible reaction,<sup>47</sup> while there is also a linear relationship between the cathodic peak current ( $i_{pc}$ ) and  $v^{1/2}$ , as seen in Figure 4c, indicating a diffusion-controlled reaction characteristic. It is known that oxygen is the main reaction species in the ORR regardless of the reaction pathways; therefore, the ORR activity is expected to be mainly governed by the mass transport of oxygen, which is closely related to the oxygen solubility and the oxygen diffusion coefficients. This relationship between the ORR potential and current with scan rate is observed in other NaOH and KOH solutions too, suggesting the reaction kinetics in different alkaline solutions is similar. Clearly, the ORR kinetics is strongly affected by the solvent environment in NaOH and KOH solutions.

In general, the peak current of the diffusion-controlled quasi-reversible electrochemical reaction at 298 K can be described by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_{O_2}^{1/2} C_{O_2} v^{1/2} \quad (9)$$



**Figure 3.** Comparison of ORR peak potentials (a) and current densities (b) in NaOH and KOH ranging from 0.5 to 14 M at 298 K. Scan rate: 100 mV/s.



**Figure 4.** (a) CV curves of a polycrystalline Pt wire electrode (diameter, 0.75 mm) at different scan rates. (b)  $\Delta E_p$  of ORR as a function of  $\nu^{1/2}$ . (c) ORR peak current as a function of  $\nu^{1/2}$  in O<sub>2</sub> saturated 1 M KOH solution at 298 K.

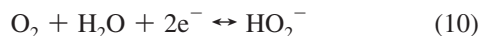
**TABLE 2: Electron Transfer Number of the ORR in NaOH and KOH Solutions at 298 K Ranging from 0.5 to 14 M**

concentration (mol L <sup>-1</sup> )	electron transfer number of ORR ( <i>n</i> )	
	NaOH	KOH
0.5		1.57
1	1.27	1.41
1.5		1.20
2	1.05	1.09
4	1.01	0.99
6	0.98	0.97
8	0.98	0.99
12	0.97	0.98
14		

where  $i_p$  is the peak current,  $n$  the number of electrons,  $F$  the Faraday constant,  $A$  the surface area of the working electrode,  $D_{O_2}$  the diffusion coefficient of the oxygen,  $C_{O_2}$  the solubility of the oxygen, and  $\nu$  the scan rate of voltammograms. In order to determine the  $n$  values, eq 9 was employed, in which the  $i_p$  data from Table 1 and the  $D_{O_2}$  and  $C_{O_2}$  data from previous studies<sup>39,40</sup> were used.

Consequently, the electron transfer number ( $n$ ) of the ORR in NaOH and KOH solution was obtained and presented in Table 2. Obviously, in both NaOH and KOH solutions, there is a transition of  $n$  from 2 in dilute solutions to 1 in concentrated solutions, suggesting the ORR reaction pathway shift from 2e reduction (as shown in eq 10) to 1e reduction

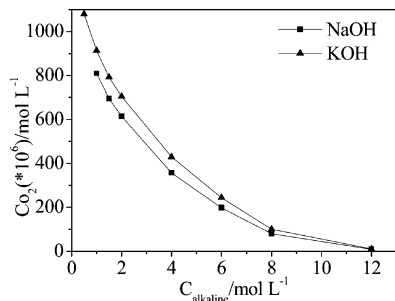
(as shown in eq 3) and the lifetime of the superoxide intermediate is extended with the increase of alkaline concentration.



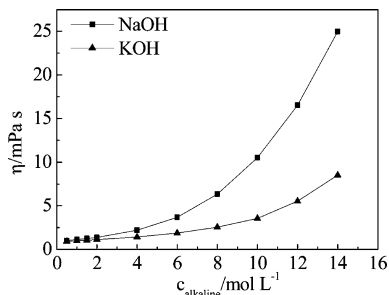
This electrolyte-dependent effect on reaction mechanisms originates from the protonation of  $O_2^-$ , as illustrated in eq 6. In basic solutions,  $H_2O$  is the proton source that reacts with  $O_2^-$  to produce  $HO_2^-$ ,<sup>19</sup> and as the alkaline concentration increases, the protonation of the superoxide reaction is significantly suppressed due to the increase of  $OH^-$  concentrations and the decrease of  $H_2O$ ; thus, the 1e ORR is dominating. This conclusion is consistent with the previous investigations in NaOH solutions.<sup>17,18</sup>

**3.4. Oxygen Solubility ( $C_{O_2}$ ) in Alkaline Solutions.** Oxygen is the reactant of the ORR, and thus, the dissolution of oxygen in alkaline solutions appears to be a main factor in ORR kinetics according to eq 9. The solubility of oxygen in aqueous alkaline solutions has been studied extensively, and  $C_{O_2}$  values in NaOH and KOH aqueous solutions at 298 K<sup>39,40</sup> are summarized and plotted in Figure 5.





**Figure 5.** Comparison of oxygen solubility between NaOH and KOH solutions at 298 K and  $P_{O_2} = 1$  atm ( $C_{O_2}$  data in NaOH were taken from Tromans,<sup>39</sup> and those in KOH were taken from Davis<sup>40</sup>).

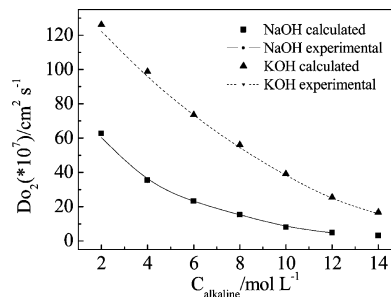


**Figure 6.** Comparison of the viscosity of NaOH and KOH solutions at 298 K.

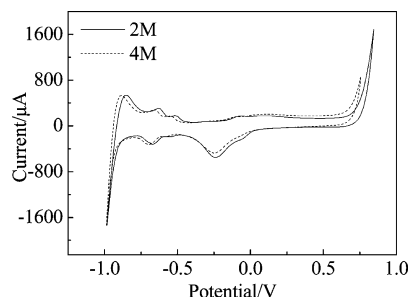
As can be seen from Figure 5, oxygen solubility in both NaOH and KOH decreases monotonically with the electrolyte concentration, and  $C_{O_2}$  in KOH solution is always higher than that in the corresponding NaOH solution. The decrease of oxygen solubility with alkaline solution concentration originates from the “salting-out effect” and can be well described using the classical Setchenow equation:<sup>48</sup>

$$\log(C_{O_2}/C_{O_2}^0) = K^s c \quad (11)$$

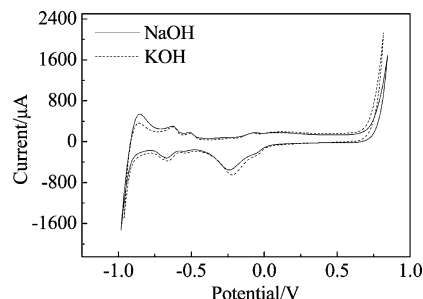
where  $C_{O_2}^0$  is the solubility of oxygen in pure water,  $C_{O_2}$  is the solubility in the presence of alkali,  $K^s$  is the Setchenow constant, and  $c$  is the alkaline concentration. The  $K^s$  values of oxygen in aqueous NaOH and KOH solutions are 0.179 and 0.175, respectively.<sup>49</sup> In  $O_2$ –MOH– $H_2O$  ( $M = Na$  or  $K$ ) systems, due to the charges the ionic species carry and the polarity the water molecules exhibit, the interactions between the ions and the water molecules are strong, inhibiting the dissolution of oxygen molecules, which are hydrophobic in nature. With the increase of electrolyte concentration, more ionic species are present in the solution and the interactions between the water and ions are strengthened, further decreasing the dissolution of oxygen molecules. The strong dependence of oxygen solubility on the complex interactions and disturbance between oxygen and media<sup>50</sup> is proposed to be the origin of the salting-out effect, and a positive  $K^s$  value is obtained.<sup>51</sup> One direct effect of the decreased oxygen solubility with alkaline concentration on the ORR is the significant reduction of reaction current density, as clearly seen in Figure 3b. Further, because potassium ion is larger in size and smaller in charge density when compared to sodium ion, the interaction between potassium ion and water is less significant than the sodium ion/water interaction. Thus, for the same electrolyte concentration, the salting-out effect to oxygen in KOH solution is weaker than that in NaOH solutions,<sup>52</sup> and in terms of ORR, the reaction



**Figure 7.** Calculated oxygen diffusion coefficients in NaOH and KOH solutions at 298 K. Experimental data: NaOH<sup>18</sup> and KOH.<sup>40</sup>



**Figure 8.** CV curves in  $O_2$ -saturated 2 and 4 M NaOH solutions at 298 K, respectively. Scan rate: 100 mV/s.



**Figure 9.** CV curves in oxygen-saturated 2 M NaOH and KOH solutions at 298 K, respectively. Scan rate: 100 mV/s.

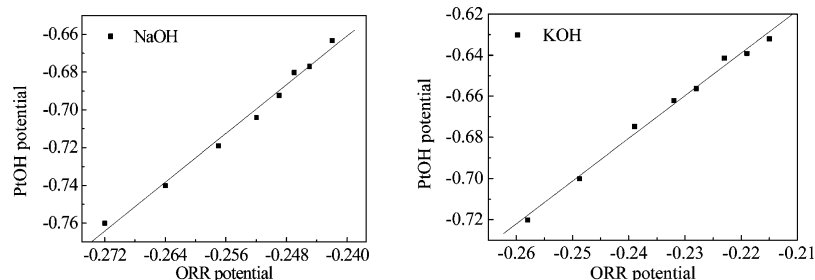
current density in NaOH solutions is smaller than that in corresponding KOH solutions, as seen in Figure 3b.

**3.5. Diffusion Coefficient ( $D_{O_2}$ ) in Alkaline Solutions.** In addition to the solubility of oxygen, the diffusivity of the dissolved oxygen is also critical to the ORR, and the oxygen diffusivity is believed to be closely related to the viscosity of the solutions.<sup>24</sup> The relationship between diffusion coefficient and solution viscosity is given by the Stokes–Einstein equation:<sup>23</sup>

$$D = kT/(6\pi r\eta) \quad (12)$$

where  $r$  is the effective hydrodynamic radius of oxygen molecule,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta$  is the solution viscosity.

The viscosities of NaOH and KOH solutions were measured at 298 K, and the results are plotted in Figure 6. As can be seen in Figure 6, the electrolyte viscosity increases monotonically with the alkaline concentration, and the viscosity of NaOH solution is larger than that of corresponding KOH solution for the same electrolyte concentration. Further, the oxygen diffusion coefficients were calculated using the viscosity data from Figure 6 and the Stokes–Einstein equation (eq 12), and the results are presented in Figure 7. In the concentration range from 2 to 14 M, the radii of dissolved oxygen molecules are approximated to be 2.8 Å<sup>18</sup> and 1.68 Å<sup>40</sup> in NaOH and KOH solutions,



**Figure 10.** Correlation between ORR peak potentials and electrolyte-dependent PtOH potentials at 298 K. Scan rate: 100 mV/s.

respectively. In Figure 7, the calculated  $D_{O_2}$  are in excellent agreement with the experimental data, confirming the dependence of  $D_{O_2}$  on electrolyte viscosity. Further,  $D_{O_2}$  in both NaOH and KOH decreases with the increase of electrolyte concentration, and  $D_{O_2}$  in KOH solution is always higher than that in the corresponding NaOH solutions. All of these observations agree with the current density change of ORR, suggesting the dependence of ORR activity on oxygen diffusivity in electrolyte solutions as described in eq 9.

**3.6. Influence of Electrochemical Reaction of Platinum on the ORR.** As previously mentioned in section 3.1, the ORR suffers from overpotential when Pt is used as the working electrode due to the electrochemical reaction of platinum, and the effect of Pt involved interaction is more appreciable with the increase of alkaline concentration. Further, from Table 1 and Figure 2, the peak potentials of the ORR in NaOH solutions are more negative than that in corresponding KOH solutions, which was proposed to be attributed to the electrolyte-dependent OH adsorption at the Pt electrode surface. In order to elucidate the effect of the Pt electrode on the ORR, the change of Pt surface adsorption reaction with electrolyte type and concentration has been studied.

Figure 8 shows the CV curves in oxygen-saturated 2 and 4 M NaOH solutions, respectively. Obviously, as the alkaline concentration increases, the peak potential of the PtOH adsorption peak negatively shifts from  $-0.627$  to  $-0.658$  V, while the ORR peak potential negatively shifts from  $-0.239$  to  $-0.243$  V. The formation of PtOH and the adsorption of  $OH^-$  at the platinum surface are sensitive to the solvent conditions,<sup>53</sup> and in alkaline solutions, instead of the water dissociation, the discharge of  $OH^-$  from supporting electrolyte is mainly responsible for the  $OH_{ads}$  accumulation.<sup>54</sup> Besides, it is evident that the negative shift of the PtOH formation potential leads to the transition from Langmuir adsorption kinetics to Temkin adsorption kinetics, intensifying the  $OH^-$  surface coverage and Pt/ $OH^-$  bond strength.<sup>55</sup> Therefore, as the electrolyte concentration increases, the PtOH adsorption is consolidated. In addition, due to the surface blockage and energetic effect,<sup>43,44</sup> the ORR is substantially sensitive to the PtOH formation. In Figure 8, with the increase of electrolyte concentration, the overpotential of ORR increases and the PtOH formation is intensified. This phenomenon exists in both NaOH and KOH solutions ranging from 0.5 to 14 M; thus, it is possible that the ORR peak potential is significantly influenced by the electrolyte-dependent PtOH adsorption.

The comparison of the CV curves in oxygen-saturated 2 M NaOH and KOH solutions was illustrated in Figure 9. The peak potentials of ORR and PtOH in KOH are  $-0.225$  and  $-0.620$  V, respectively, while the corresponding potentials are  $-0.239$  and  $-0.627$  V in NaOH solution. The more positive ORR and PtOH potentials in KOH solution indicate that, compared with the NaOH solution, KOH solution is a superior reaction media

for the ORR and the platinum oxidation/reduction reactions thermodynamically.

Further, it is interesting to see in Figure 10, which describes the relations between the ORR potentials and PtOH potentials, that there is a linear relationship between ORR peak potentials and electrolyte-dependent PtOH potentials in both NaOH and KOH solutions ranging from 0.5 to 14 M. This is possibly due to the increased bond strength and surface coverage of PtOH groups with the increase of the alkaline concentrations, blocking the active sites and altering the energy for the adsorption of  $O_2$  and further the formation of reduced oxygen species. Consequently, the ORR process has been frustrated and the overpotential loss has been increased.

#### 4. Conclusions

In this paper, the ORR in NaOH and KOH solutions has been compared from 0.5 to 14 M by using cyclic voltammetry. It is observed that, for ORR, KOH solutions are superior to NaOH solutions in both kinetic and thermodynamic considerations, and the ORR performance frustrates as the concentration increases in both alkaline solutions.

The electrochemical oxygen reduction in NaOH and KOH solutions is attributed to a quasi-reversible diffusion-controlled reaction. Both the ORR mechanisms and kinetics are largely determined by the electrolyte conditions in the NaOH and KOH solutions. As the alkaline concentration increases, the protonation of superoxide is suppressed; thus, the ORR shifts from a 2e reduction pathway to a 1e reduction pathway in both solutions. Besides, the ORR kinetics is affected by the oxygen solubility, oxygen diffusivity, and PtOH formation. The electrolyte-dependent oxygen solubility and diffusivity are responsible for the change of ORR activity with concentration and electrolyte species, while the ORR is substantially affected by the electrochemical reaction of platinum due to the connection between the ORR and electrolyte-dependent PtOH formation.

In summary, it is concluded that the ORR process is substantially determined by the electrolyte conditions in NaOH and KOH solutions. This electrolyte-dependent effect, which consists of the behavior of oxygen and the reaction intermediate discharged from electrolyte, originates from the interaction among the oxygen, salt ions, water, and electrode. The electrolyte with high oxygen solubility, low viscosity, and weak adsorption species will greatly improve the ORR.

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