

# Cathodic reaction kinetics and its implication on flow-assisted corrosion of aluminum alloy in aqueous ethylene glycol solution

Y. Liu · Y. F. Cheng

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**Abstract** The cathodic reaction kinetics and anodic behavior of Al alloy 3003 in aerated ethylene glycol–water solution, under well-controlled hydrodynamic conditions, were investigated by various measurements using a rotating disk electrode (RDE). The transport and electrochemical parameters for cathodic oxygen reduction were fitted and determined. The results demonstrate that the cathodic reaction is a purely diffusion-controlled process within a certain potential region. The experimentally fitted value of diffusion coefficient of oxygen is  $3.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . The dependence of cathodic current on rotation speed was in quantitative agreement with Levich equation. At potentials more positive than the diffusion controlled region, the cathodic process was controlled by both diffusion and electrochemical kinetics. The electrochemical reaction rate constant,  $k_0$ , was determined to be  $1.1 \times 10^{-9} \text{ cm s}^{-1}$ . There is little effect of electrode rotation on anodic behavior of Al alloy during stable pitting. However, fluid hydrodynamics play a significant role in formation of the oxide film and the Al alloy passivity. An enhanced electrode rotation would increase the mass-transfer rate of solution, and thus the oxygen diffusion towards the electrode surface for reduction reaction. The generated hydroxide ions are favorable to the formation of Al oxide film on electrode surface.

**Keywords** Electrochemical corrosion · Aluminum alloy · Cathodic process · Ethylene glycol · Fluid hydrodynamics

## 1 Introduction

It has been acknowledged [1, 2] that corrosion resistance of aluminum (Al) alloy is dependent on the formation of a layer of oxide film on its surface. Al alloys, due to their good formability and excellent heat efficiency, have been used widely in various industrial applications [3]. However, the environmental factors including an elevated temperature, a strong alkalinity, the presence of halide ions and a high fluid flow velocity [4, 5] could damage, thinner or evenly complete remove the film and enhance corrosion of Al alloy significantly. In automobile cooling system, Al alloy heat exchanger pipe has encountered flow-assisted corrosion (FAC) due to the presence of chloride ions in the flowing coolant (mainly ethylene glycol) [3].

Corrosion of Al alloy has been studied extensively in various aqueous solutions, and theories and models have been developed to illustrate corrosion, especially pitting corrosion, of Al [1]. However, to date, there has been few work performed in ethylene glycol–water solution to investigate corrosion of Al alloy in automobile cooling system. In the previous work, Niu and Cheng [6] studied the electrochemical corrosion behavior of 3003 Al alloy in ethylene glycol–water solution, and concluded that, in the presence of oxygen, a layer of oxide film forms on Al electrode surface to protect the substrate from corrosion. In the absence of oxygen, the film formed is mainly aluminum alcohol film that is less compact and less resistant to corrosion. Furthermore, they used rotating disk electrode (RDE) and rotating cylinder electrode (RCE) to study the effects of fluid hydrodynamics on Al corrosion [7]. It was found that the Al corrosion is mixed-controlled by both activation and diffusion steps at low and intermediate electrode rotating speeds. When the rotating speed is sufficiently high, there is a synergistic effect of fluid

Y. Liu · Y. F. Cheng (✉)  
Department of Mechanical & Manufacturing Engineering,  
University of Calgary, Calgary, AB T2N 1N4, Canada  
e-mail: fcheng@ucalgary.ca

hydrodynamics and sand particles on Al erosion–corrosion (E–C) when the solution contains solid sands.

Cathodic process, which is an essential part of corrosion reaction, is usually ignored in investigation of metallic corrosion. During corrosion of Al alloy, cathodic reaction, i.e., reduction of the dissolved oxygen, is expected to play a critical role in corrosion of Al alloy. In this work, cathodic reaction kinetics and anodic behavior of Al alloy in ethylene glycol–water solution were studied by RDE technique. It is anticipated that this research provides an essential insight into the mechanism of Al alloy corrosion in automotive coolant.

## 2 Experimental

Rotating disk electrodes of 6 mm in diameter were made of 3003 Al alloy, supplied by DANA Canada Corporation, with a chemical composition (wt.%): Cu 0.20, Fe, 0.70, Si 0.60, Mn 1.50, Mg 0.05, Cr 0.05, Zn 0.10, Ti 0.05, and Al balance. The unexposed faces and edges of RDE were sealed with Teflon epoxy. Before tests, the working surface of the electrode was ground with 800 and 1200 grit silicon carbide papers, polished with a 1 micron alumina paste, and then cleaned by deionized water and acetone.

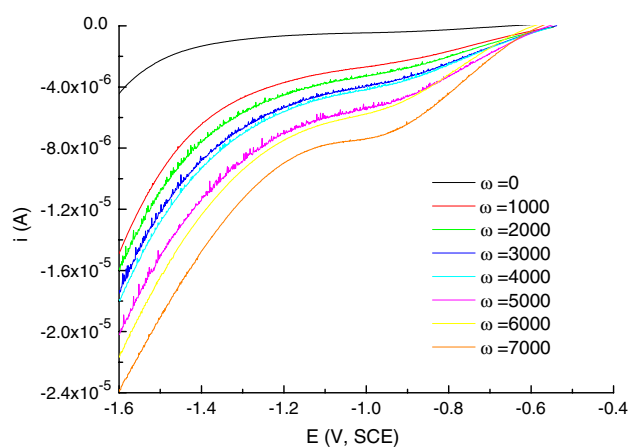
The test solution was a 50% ethylene glycol + 50% deionized water + 100 ppm  $\text{Cl}^-$  solution to simulate the automotive coolant. All solutions were made from analytic grade reagents and ultra-pure deionized water (18 M $\Omega$  cm). All the tests were conducted at the ambient temperature (20  $\pm$  0.2  $^\circ\text{C}$ ).

Electrochemical measurements were performed using a three-electrode cell, with Al RDE as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode. Polarization curves were measured through a PAR Model 263A Potentiostat/Galvanostat. The electrode rotation was controlled by a Pine AFM-SRX rotator system. Linear sweep voltammetry tests were performed at a potential sweep rate of 10 mV/s. In potentiostatic current transient tests, the Al RDE was potentiostatically controlled and the current density was recorded as a function of electrode rotating speed that was stepped up with time.

## 3 Results

### 3.1 Cathodic voltammograms of Al RDE

Figure 1 shows the cathodic voltammograms of Al RDE at the various rotating speeds. It is seen that, under the static condition, the reductive current density decreased with the positive shift of potential until  $-1.4$  V (SCE). The

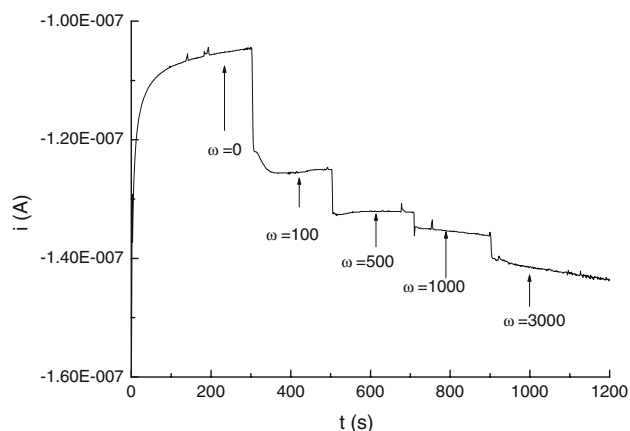


**Fig. 1** Cathodic polarization curves of Al alloy RDE under various rotating speeds

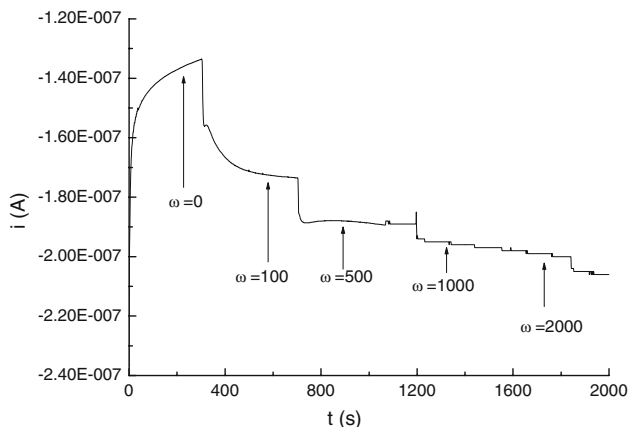
reductive current density was then maintained at a relatively steady value over the remaining potential range. Upon electrode rotation, the reductive current density increased significantly. Moreover, the current density increased with the increasing electrode rotating speed. Furthermore, with the positive shift of applied potential, the reductive current density decreased, then experienced a plateau at approximately  $-1.1$  V  $\sim$   $-1.0$  V (SCE), and finally decreased rapidly to zero when the potential approached corrosion potential. The current density plateau phenomenon was more apparent at a higher electrode rotating speed.

### 3.2 Potentiostatic cathodic current transient measurements of Al RDE

Figures 2 and 3 show the cathodic current transient curves measured on Al RDE at  $-0.7$  V and  $-0.75$  V (SCE), respectively. The two potential values were within the



**Fig. 2** Cathodic current transient measurements of RDEs at the potential of  $-0.7$  V (SCE)

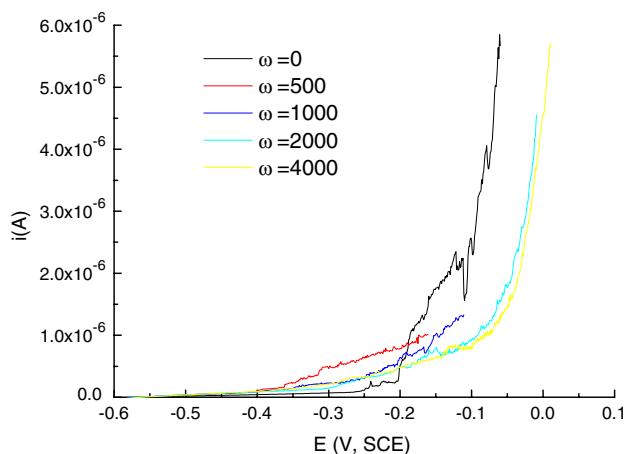


**Fig. 3** Cathodic current transient measurements of RDE at potential of  $-0.75$  V (SCE)

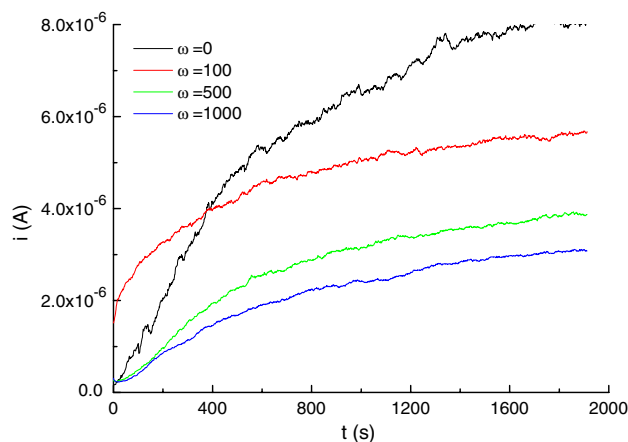
cathodic Tafel region, as seen in Fig. 1. It is seen that, at both applied potentials, the cathodic current density dropped rapidly to a more negative value upon the increase of electrode rotating speed, and then reached a steady value. Moreover, with the increase in electrode rotating speed, the steady cathodic current density increased.

### 3.3 Anodic voltammogram measurements

Figure 4 shows the anodic voltammograms of Al RDE as a function of electrode rotating speed. It is seen that anodic current density increased with the positive shift of potential. To further investigate the dependence of anodic current density on electrode rotating speed, potentiostatic measurements were performed. Figure 5 shows the potentiostatic anodic polarization measurements of Al RDE at  $-0.5$  V (SCE) under the various electrode rotating speeds. It is apparent that the steady state current intensity decreased with the increase of electrode rotating speed, with some irregular changes of current density in the first 400 s.



**Fig. 4** Anodic polarization curves of Al alloy RDE under various rotating speeds



**Fig. 5** Potentiostatic anodic polarization measurements of Al alloy RDE at potential of  $-0.5$  V (SCE)

## 4 Discussion

### 4.1 Purely diffusion-controlled cathodic reaction kinetics

The cathodic process during Al corrosion in aerated ethylene glycol–water solution is dominated by diffusion of the dissolved oxygen towards the Al electrode surface and then the reduction of oxygen by:



Apparently, an increase of electrode rotating speed would accelerate the diffusion of oxygen towards the electrode for cathodic reduction reaction, resulting in an increase of cathodic reductive current density (Fig. 1). The presence of a current density plateau in cathodic polarization curve indicates that diffusion of oxygen towards the electrode surface acts as the rate-controlling step of the cathodic reaction. According to Levich equation [8], a purely diffusion-controlled electrode reaction process occurring on a RDE surface is characterized as:

$$i_L = 0.62nAFD^{2/3}\omega^{1/2}\nu^{-1/6}C_0 \quad (2)$$

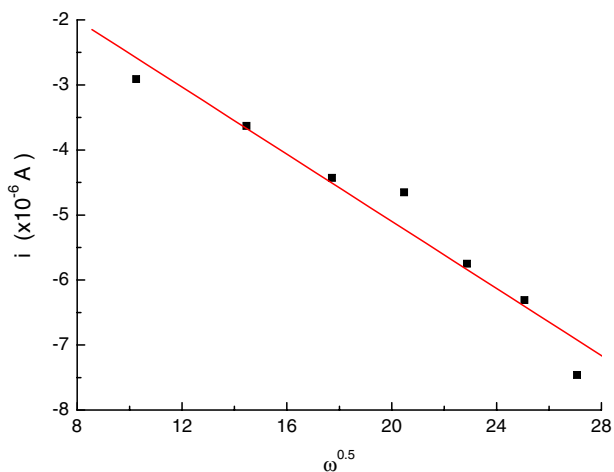
where  $i_L$  is the steady-state limiting diffusive current density,  $n$  is stoichiometric number of electrons exchanged in the reaction,  $A$  is electrode area,  $F$  is Faraday constant,  $D$  is diffusion coefficient,  $\omega$  is angular rotating velocity of RDE,  $\nu$  is kinematic viscosity of the solution, and  $C_0$  is the bulk concentration of the electroactive species. It is worthy pointing out that the angular velocity of RDE should be limited in the range of  $10 \text{ s}^{-1} < \omega < 1000 \text{ s}^{-1}$  since the Levich equation applies for the laminar flow only [9]. It is apparent from the equation that the cathodic limiting diffusive current density is proportional to the square root of angular velocity for a purely diffusion-controlled reaction.

The measured limiting diffusive current density at the individual electrode rotating speed (in both rpm and  $\text{rad s}^{-1}$ ) is shown in Table 1. Figure 6 shows the relationship between the measured  $i_L$  and  $\omega^{1/2}$ . A well-fitted linear relationship is observed. It is further demonstrated that cathodic process in Al corrosion is a purely diffusion-controlled process.

From the slope of the fitted straight line, diffusion coefficient of oxygen in the test solution can be obtained. The values and unites of input parameters in the present system are listed in Table 2. Since the calculated diffusivity is based on the fitting of the measured cathodic polarization curve, and the cathodic reaction is dominated by reduction of oxygen in aerated, near-neutral pH solution, it is thus ascertain that the diffusivity of  $\text{O}_2$  is

**Table 1** Electrode rotating speed and limiting diffusive current of RDE under controlled laminar condition

$\omega$ (rpm)	$\omega$ (rad./s)	$i_L$ ( $\times 10^{-6}$ A)
1000	105	-2.91
2000	209	-3.63
3000	314	-4.43
4000	419	-4.65
5000	523	-5.75
6000	628	-6.31
7000	733	-7.46



**Fig. 6** Limiting diffusive current of oxygen reduction as a function of the square root of RDE angular rotating velocity

**Table 2** Values and unites of input parameters for fitting and determination of diffusion coefficient of oxygen

$n$	$A$ ( $\text{cm}^2$ )	$F$ (C/mol)	$\nu$ ( $\text{cm}^2/\text{s}$ )	$C_0$ (mol/L)
4	0.2826	96500	0.0203	$2.1 \times 10^{-4}$

measured in this work. The experimentally fitted value of diffusion coefficient ( $D$ ) of oxygen in ethylene glycol–water solution is  $3.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ .

In addition to diffusivity of oxygen, some other important hydrodynamic parameters that are essential to cathodic and anodic reactions can be determined from the measurements of cathodic limiting diffusive current density, such as mass-transfer coefficient ( $k_m$ ), thickness of diffusion layer ( $\delta$ ), Sherwood number ( $Sh$ ) and Schmidt number ( $Sc$ ). The formulas for calculation of the parameters are shown as [8]

$$k_m = \frac{i_L}{nAFC} \quad (3)$$

$$\delta = 1.61D^{1/3}\omega^{-1/2}\nu^{1/6} \quad (4)$$

$$Sh = \frac{k_m r}{D} \quad (5)$$

$$Sc = \frac{\nu}{D} \quad (6)$$

where  $r$  is the radius of RDE. Furthermore, Reynolds number ( $Re$ ) is usually used to quantify the fluid flow condition, and is determined by the geometry of electrode, fluid velocity and kinematic viscosity of solution by

$$Re = \frac{\omega r^2}{\nu} \text{ (for RDE)} \quad (7)$$

The values of all parameters are determined and listed in Table 3.

Experimental Sherwood dimensionless group correlation for RDE is defined as:

$$Sh = aRe^b Sc^{0.33} \quad (8)$$

Re-organize Eq. 8:

$$\log\left(\frac{Sh}{Sc^{0.33}}\right) = b \log Re + \log a \quad (9)$$

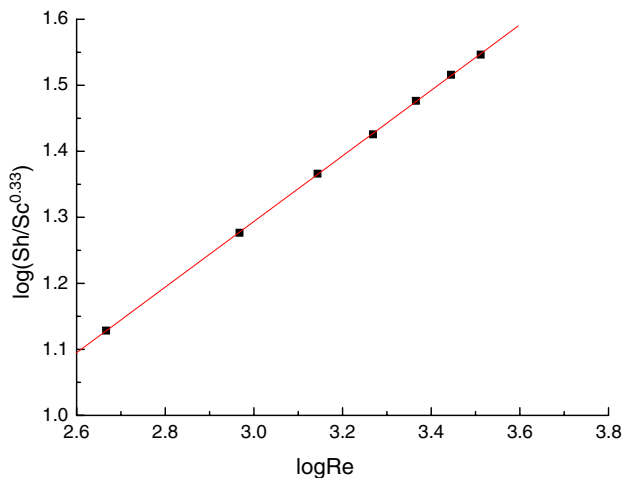
Therefore, there is a linear relationship between the logarithm of  $\left(\frac{Sh}{Sc^{0.33}}\right)$  and the logarithm of  $Re$ . Use the determined values in Table 3 and make a plot in Fig. 7, and the coefficients,  $a$  and  $b$ , can be obtained from the line:  $a = 0.636$ , and  $b = 0.497$ . Therefore, the Sherwood dimensionless group correlation for mass-transfer of oxygen in glycol–water solution is determined as

$$Sh = 0.636Re^{0.497} Sc^{0.33} \quad (10)$$

Furthermore, the fitted values of  $a$  (0.636) and  $b$  (0.497) in this work are comparable to the theoretical values according to Levich equation, where  $a = 0.62$  and  $b = 0.5$  [9, 10]. The approximation of the constants supports the conclusion that the plateau in cathodic polarization curve is due to diffusion of cathodic reactant, i.e., oxygen.

**Table 3** Hydrodynamic parameters obtained for Al alloy RDE in ethylene glycol–water solution under controlled laminar condition

$\omega$ (rpm)	$\omega$ (rad./s)	$Re$	$k_m$ ( $\times 10^{-4}$ cm/s)	$\delta$ ( $\times 10^{-4}$ cm)	$Sh$	$Sc$
1000	105	464	1.18	2.55	1180	$6.77 \times 10^5$
2000	209	928	1.66	1.81	1660	
3000	314	1392	2.04	1.47	2040	
4000	419	1856	2.34	1.28	2340	
5000	523	2320	2.63	1.14	2630	
6000	628	2784	2.88	1.04	2880	
7000	733	3248	3.09	0.97	3090	



**Fig. 7** Derivation of the Sherwood dimensionless group correlations for oxygen mass transfer in ethylene glycol–water solution under controlled laminar condition

#### 4.2 Cathodic reaction kinetics under mixed control

With the positive shift of cathodic potential, the cathodic process shows a mixed-controlled behavior, which is confirmed by potentialstatic current transient measurements in Figs. 2 and 3. When RDE is used to investigate a mixed-controlled reaction, the Koutecky–Levich equation is usually applied to separate the measured currents that are attributed to mass-transfer step and charge-transfer step, respectively:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{zFAC_0k_0 \exp(-\alpha zF\eta/RT)} + \frac{1}{0.62nAFD^{2/3}\omega^{1/2}v^{-1/6}C_0} \quad (11)$$

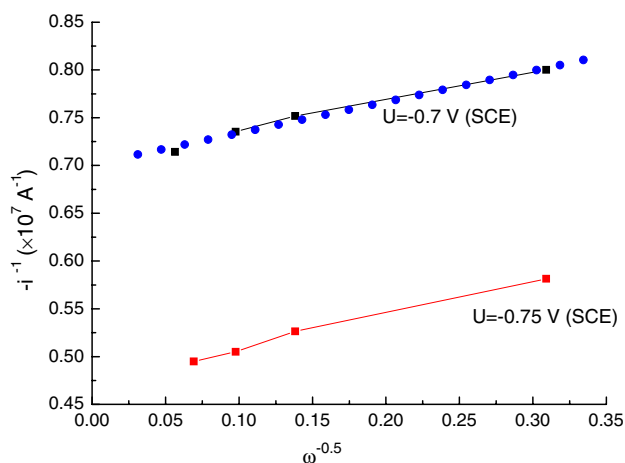
where  $i_K$  is the current intensity in the absence of mass-transfer effect,  $k_0$  is the potential-independent electrochemical rate constant,  $\alpha$  is charge-transfer coefficient,  $R$  is the molar gas constant,  $T$  is temperature, and  $\eta$  is over-potential. Other parameters have the identical meaning to the previous description.  $z$  in Eq. 11 is the

stoichiometric number of electrons exchanged in charge-transfer step. According to the reported works [11, 12], the charge-transfer controlled step for oxygen reduction is a one-electron transfer process:



Thus, the stoichiometric number of electrons exchanged,  $z$ , is equal to 1. As shown in Fig. 8, the purely charge-transfer controlled current density,  $i_K$ , can be obtained by extrapolating  $i^{-1}$  to an infinitely high mass-transfer rate, where charge-transfer is expected to dominate the cathodic process. It is seen from Fig. 8 that, when potential is shifted positively from  $-0.75$  V (SCE) to  $-0.70$  V (SCE), the purely charge-transfer controlled current density decreases, indicating that the oxygen reduction is inhibited at a less negative potential. According to Eq. 11, determination of  $i_K$  upon the extrapolation of  $i^{-1}$  at various potentials allows calculations of  $k_0$ . The electrochemical reaction rate constant,  $k_0$ , is determined to be  $1.1 \times 10^{-9}$  cm s $^{-1}$ .

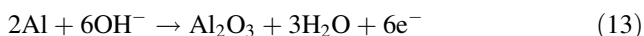
At potentials less than the plateau potentials on the cathodic curve in Fig. 1, the cathodic reaction is mainly reduction of hydrogen ions. It is a typical activation-controlled cathodic process.



**Fig. 8** Koutecky–Levich plots for mixed-controlled electrode reaction on Al RDE

### 4.3 Effects of cathodic oxygen reduction on corrosion of Al alloy

Anodic behavior of Al alloy in aerated ethylene glycol–water solution is presented in Fig. 4, where the extremely low current density region up to about  $-0.35$  V (SCE) refers to passivity of Al alloy. It has been acknowledged [13] that the good corrosion resistance of Al alloys is due to the formation of a layer of oxide film on electrode surface by



In the presence of chloride ions, they may penetrate into the defects of  $\text{Al}_2\text{O}_3$  film and replace oxygen, generating cation vacancies at the film/solution interface [14]. A flux of cation vacancies across the film to the film/metal interface is thus resulted in. If the cation vacancy flux is so high that the cation vacancies cannot be annihilated at the metal/film interface, a cation vacancy condensate will be formed, causing the thinning of film or the local detachment from the metal. A pit is then generated at the location where chloride ions absorb. At low anodic potentials, the pit initiation and its repassivation compete each other, causing current oscillation, as shown in Fig. 4. At a sufficiently high anodic potential, metastable pitting develops into stable pitting, resulting in a significant increase of anodic current density.

There is little effect of electrode rotation on anodic behavior of Al alloy during stable pitting. However, fluid hydrodynamics play a significant role in the formation of oxide film. As seen in Fig. 5, at a high electrode rotating speed, a low anodic current density is resulted in. Apparently, an enhanced electrode rotation would increase the solution hydrodynamics, and thus the oxygen diffusion towards the electrode surface for reduction reaction [15, 16]. The generated hydroxide ions are favorable to the formation of Al oxide film on electrode surface. The initial irregularity of current density in the first 400 s in Fig. 5 is probably attributed to the slight difference of electrode surface status at the different tests. After a steady-state is achieved, the initial difference in electrode surface condition will be offset by a stable electrode state, which depends on the various electrode rotating speeds.

## 5 Conclusions

An increase of electrode rotating speed would accelerate the diffusion of oxygen towards the electrode surface for

cathodic reduction reaction, resulting in an increase in cathodic reductive current density. The cathodic reaction is a purely diffusion-controlled process in aerated, ethylene glycol–water solution. The experimentally fitted diffusion coefficient of oxygen is  $3.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . The dependence of cathodic current on rotation speed was in quantitative agreement with Levich equation. The Sherwood dimensionless group correlation for mass-transfer of oxygen is  $Sh = 0.636Re^{0.497}Sc^{0.33}$ .

At potentials more positive than the diffusion controlled region, the cathodic process was controlled by both diffusion and electrochemical kinetics. The electrochemical reaction rate constant,  $k_0$ , is determined to be  $1.1 \times 10^{-9} \text{ cm s}^{-1}$ .

There is little effect of electrode rotation on anodic behavior of Al alloy during stable pitting. However, fluid hydrodynamics play a significant role in formation of the oxide film and the Al alloy passivity. An enhanced electrode rotation would increase the oxygen diffusion towards the electrode surface for reduction reaction. The generated hydroxide ions are favorable to the formation of Al oxide film on electrode surface.

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