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The Effect of the Tribromide Complex Reaction on the Oxidation/Reduction Current of the Br_2/Br^- Electrode

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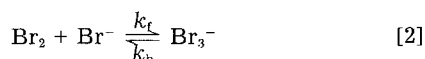
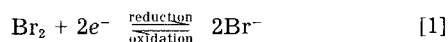
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ABSTRACT

The Br_2/Br^- electrode reaction with tribromide complex formation reaction in the solution, a chemical-electrochemical (C-E) type reaction, has been investigated in order to determine the effect of the chemical reaction on the electrode kinetics. It is shown that the chemical reaction has little effect on the electrode kinetics at very slow homogeneous reaction rates, but has a more drastic effect on the electrode kinetics at faster homogeneous reaction rates. Also, the kinetics at the electrode are affected by changes in the concentrations of the active species (Br_2 , Br^- , and Br_3^-) in the bulk solution as a consequence of the coupling effect of the chemical reaction on the electrode kinetics.

The Br_2/Br^- electrode reaction is a version of a chemical-electrochemical (C-E) reaction in which the homogeneous chemical step in reaction [2] precedes the charge-transfer step in reaction [1]



This reaction has attracted considerable attention in the past couple of years (1-5) because it serves as one of the principal electrode reactions of the Zn/ Br_2 secondary battery system that is being considered for use in large scale energy storage. Information about this reaction is desired to aid in the design and optimization of the Zn/ Br_2 battery.

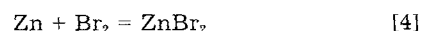
The equilibrium constant for reaction [2], K_{eq} , where $K_{\text{eq}} = k_f/k_b$, is only 17.0 liters/mol (6). As a result, significant concentrations of Br_2 , Br^- , and Br_3^- will commonly be present in the electrolyte. For that matter, any detailed model for predicting the current-potential characteristics of the Br_2/Br^- electrode must include the effects of the homogeneous complexation reaction. In the past, some investigators (7) have justified the exclusion of the chemical reaction by assuming the complexation kinetics to be very rapid. In other words, they considered this reaction to be essentially at equilibrium at all points in the electrolyte and for this reason assumed that the chemical reaction had no effect on the electrode kinetics. Other investigators (8, 9) were able to account for the effect of the chemical reaction on the electrode kinetics by considering the equilibrium constant of the chemical reaction to be independent of distance from the electrode surface. With the latter approach, Newman (9) demonstrated with the $\text{CuSO}_4\text{-H}_2\text{SO}_4$ system that the incomplete dissociation of the homogeneous bisulfate reaction did have a dramatic effect on the limiting currents as a result of changes in the ionic strength of the solution due

to the migration of dissociated species. However, for cases with moderate or slow homogeneous kinetics, the assumption that the homogeneous reaction is at equilibrium at all points in the electrolyte is no longer valid. Therefore, a more realistic approach must be adopted to account for the effect of this homogeneous reaction on the electrode kinetics. This involves treating the chemical reaction as a reaction with a finite rate, where the pseudo-equilibrium constant for this system, $K'(\zeta)$, is defined as

$$K'(\zeta) = \frac{c_{\text{Br}_3^-}(\zeta)}{c_{\text{Br}^-}(\zeta)c_{\text{Br}_2}(\zeta)} \quad [3]$$

and where $K'(\zeta)$ is assumed to be a function of the normal dimensionless distance ζ from the rotating disk surface. Since the rate constants (k_f and k_b) for the chemical reaction in Eq. [2] are not known, both small and large values of these rate constants will be assumed in order to evaluate the effect of slow and fast homogeneous kinetics on the electrode kinetics. In addition, well-supported solutions will be used in order to minimize the effect of migration on the electrode kinetics.

For the Br_2/Br^- electrode, the high solubility of Br_2 in aqueous electrolytes, that is 0.21 mol/liter in water and 1.35 mol/liter in 1M KBr solution at 25°C (10), places a severe limitation on its potential applications, especially as pertains to Zn/ Br_2 battery. The high solubility of Br_2 has a detrimental effect on the turn-around efficiency of this battery system as a result of the self-discharge reaction in Eq. [4], which is promoted by the diffusion of Br_2 from the Br_2/Br^- compartment to Zn electrode



Most of the methods (2-4) designed to reduce the activity of Br_2 in the electrolyte during charge directly affect the equilibrium of the tribromide complex reaction in the bulk solution. In order to optimize the charge/discharge characteristics of the Zn/ Br_2 battery, it is of interest to determine how changes in the bulk concentrations of the

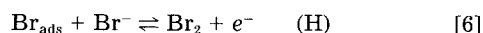
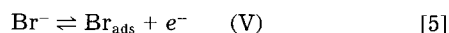
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species participating in reaction [2] will affect the anodic/cathodic current of this electrode.

In this paper, we report results obtained by simulating the current/potential characteristics of the Br_2/Br^- reaction at a rotating disk electrode using the model of Adanuvor *et al.* (12). Specifically, the reduction of Br_2 and the oxidation of Br^- are reported (11) in the presence of Br^- and Br_2 , respectively, in the concentration range where (i) Br_3^- was the dominant bromine containing species, such as is typical in the Zn/Br_2 battery and (ii) Br_3^- species was negligible. These are investigated under conditions of both slow and rapid homogeneous tribromide formation rates in order to determine the effect of the rate of the complexation reaction on the electrode kinetics and also, the effect of the concentration of the active species participating in the complexation reaction on the electrode kinetics. The data of Mastragostino and Gramelli (5) for the kinetics study of Br_2/Br^- in aqueous system on vitreous carbon electrodes were used in the investigation.

Results and Discussion

In this reaction system, the kinetic mechanism most commonly proposed for the electrochemical step in Eq. [1] is the discharge-electrochemical desorption mechanism (6, 13) often referred to as the Volmer-Heyrovsky (V-H) mechanism given by Eq. [5] and [6], respectively



The chemical step preceding the charge-transfer step is represented by the tribromide complexation reaction in Eq. [2] in the solution phase. The current density expressions derived by Lorimer (13, 14) on the basis of the V-H mechanism were used in this work. The mathematical model for this system was based on the electrode kinetics, the tribromide complexation reaction in the bulk solution, and the mass transport processes occurring in the solution (12). Table I is a list of parameter values used to obtain the results.

For slow homogeneous reaction rates, the tribromide complex formation reaction will not be in equilibrium in the region adjacent to the electrode surface as a result of the consumption/production of Br_2 or Br^- species in the electrode reaction. This effect is demonstrated in Fig. 1 where the departure from equilibrium as indicated by the values of the ratio of $K'(\zeta)$ to the equilibrium constant K_{eq} are plotted against ζ . In the bulk solution (as $\zeta \rightarrow 2$, bulk conditions are assumed to exist at twice the diffusion layer thickness), the homogeneous reaction is in equilibrium but close to the electrode surface ($\zeta \rightarrow 0.0$) there is a significant departure from equilibrium as a result of the depletion or production of Br_2 or Br^- species in the electrode reaction. As the homogeneous reaction rate increases (increasing k_f with a corresponding increase in k_b , since $k_b = k_f K_{\text{eq}}$), the region of departure from equilibrium decreases, and as shown in Fig. 1, at high k_f ($> 10^6 \text{ cm}^6/\text{mol}\cdot\text{s}$), the ratio $K'(\zeta)/K_{\text{eq}}$ is essentially equal to one throughout the solution phase until very close to the electrode surface where there is a slight deviation from equilibrium conditions. The deviation from equilibrium

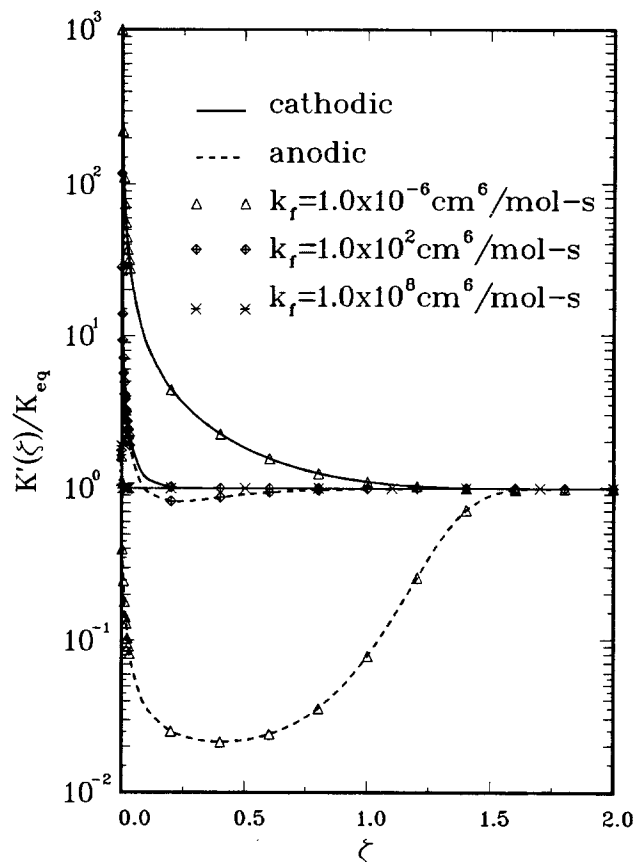


Fig. 1. Variation of the pseudo-equilibrium ratio $K'(\zeta)/K_{\text{eq}}$ with distance from the electrode surface for the Br_2/Br^- electrode. $c_{\text{Br}_2} = 4.6 \times 10^{-2} \text{ M}$, $c_{\text{Br}^-} = 0.5 \text{ M}$, and $c_{\text{Br}_3^-} = 0.001 \text{ M}$, respectively.

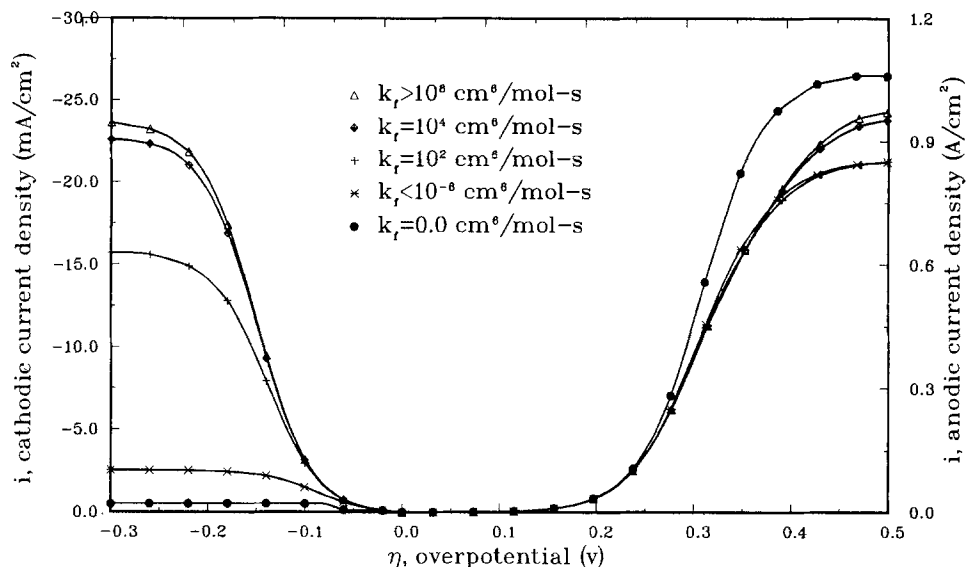
conditions persists up to a value of $k_f = 10^8 \text{ cm}^6/\text{mol}\cdot\text{s}$ for which the region close to the electrode surface where the deviation occurs is within one-hundredth of the diffusion layer thickness. At extremely high k_f values ($\geq 10^{10} \text{ cm}^6/\text{mol}\cdot\text{s}$) when the homogeneous reaction occurs at a much faster rate than the electrode reaction the pseudo-equilibrium constant becomes independent of position, ζ . As indicated in Fig. 1, much larger deviations from equilibrium conditions are obtained at slow homogeneous kinetics than at high homogeneous kinetics. From Fig. 2, it can be established that the influence of the homogeneous reaction on the electrode kinetics is more pronounced at higher values of the homogeneous kinetic rate constant especially for cathode currents. The higher the homogeneous rate constants, the more rapidly equilibrium is established for this reaction and the less the deviation from equilibrium conditions with distance from the electrode surface. This result is in agreement with the results of Pleskov and Filinovskii (11) who proposed the idea of the reaction layer thickness μ_c as a measure of the region of the rotating disk electrode where the chemical equilibrium is appreciably disturbed. They found out that in case of fast chemical reactions ($\mu_c \ll$

Table I. Parameter values^a for simulating the charge/discharge characteristics of the Br_2/Br^- electrode

Parameters	Br_2 oxidation/ reduction	Br^- oxidation/ reduction	Br_3^- oxidation/ reduction
$i_{\text{oref,H}}, i_{\text{oref,V}}$ (mA/cm ²)	0.065, 0.070	0.024, 0.054	0.065, 0.070
$\alpha_{\text{c,H}}, \alpha_{\text{c,V}}$	0.24, 0.85	0.24, 0.85	0.26, 0.84
$c_{\text{Br}_2,\infty}$ (M)	$(4.6 \times 10^{-5} - 0.023)$	0.50	0.001
$c_{\text{Br}^-,\infty}$ (M)	0.5	0.005-1.0	0.5
$c_{\text{Br}_3^-,\infty}$ (M)	0.0, 0.001	0.0, 0.001	0.0001-1.0
$c_{\text{NaClO}_4,\infty}$ (M)	0.5	0.5	0.5
$c_{\text{I}_2,\text{ref}}$ (M)	4.60×10^{-5}	0.5	0.001
k_f (cm ⁶ /mol·s)	10^{12}	10^{12}	10^{12}
Ω (rpm)	3000.0	3000.0	3000.0
ν (cm ² /s)	0.01	0.01	0.01

^a Values taken or estimated from Ref. (5).

Fig. 2. Effect of increasing k_f on Br_2/Br^- electrode kinetics under conditions where Br_3^- is the dominant Br_2 containing species. $c_{\text{Br}_2} = 4.6 \times 10^{-2}\text{M}$, $c_{\text{Br}^-} = 0.5\text{M}$, and $c_{\text{Br}_3^-} = 0.001\text{M}$, respectively.



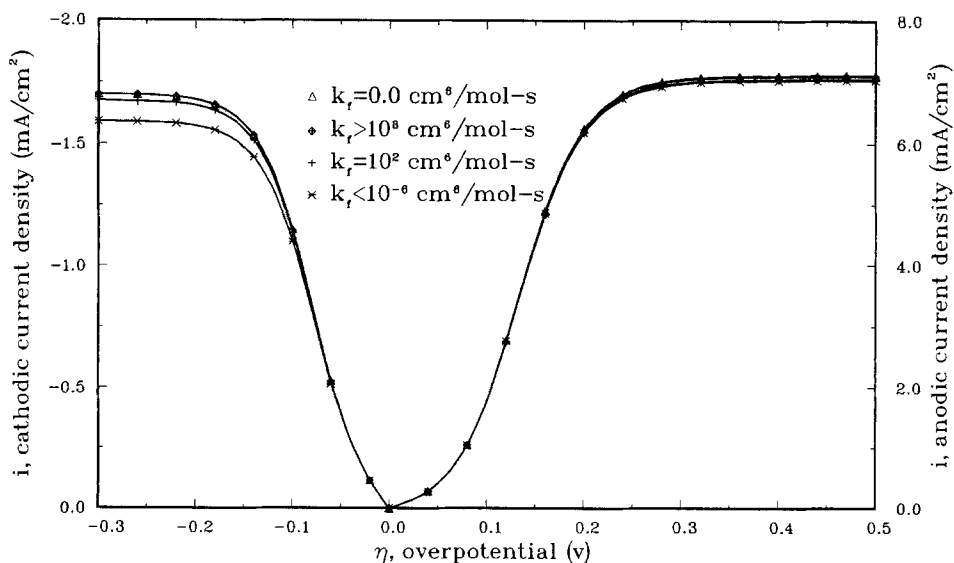
δ_D), the thickness of the reaction region is much less than that of the diffusion boundary layer. In Fig. 1, this corresponds to $\zeta \ll 1$. On the other hand, for slow chemical kinetics when $\mu_c \gg \delta_D$ as is the case in Fig. 1 when $k_f \leq 1.0 \times 10^{-6}$, the chemical reaction has usually very little effect on the electrode kinetics.

The effect of the rate of the tribromide reaction on the oxidation/reduction current of the Br_2/Br^- electrode is demonstrated in Fig. 2 for the case of a normal operating Zn/ Br_2 cell where concentrated bromide solutions are used and where Br_3^- is the dominant bromine containing species. In this system, the Br_3^- species reacts according to Eq. [2] to produce more Br_2 which undergoes further reduction at the electrode to enhance the cathodic current density. The higher the k_f value, the faster the rate of generation of Br_2 and the higher the cathodic current density. On the contrary, the anodic limiting current density relative to the current density in the absence of the complexation reaction remains unchanged at low k_f values, exhibits a depression at intermediate values, and increases at high k_f values to a value approaching that obtained in the absence of the complexation reaction. From Fig. 2, the Tafel segment of the polarization curves at various values of k_f , when corrected for the contribution due to mass transport, yield the same values for the Tafel constants (13). This limits the contribution of the homogeneous reaction on the electrode kinetics to the limiting current region. The same observation was made for the case in Fig. 3 where low concentrations of bromide solutions were used. This is not surprising since

the electrode kinetics are rather fast [i.e., exchange current densities on the order of milliamperes per square centimeter (17)]. Thus, the reaction rates at the electrode are dictated by mass transport of reacting species from the bulk solution to the electrode surface. The effect of the homogeneous reaction rate on the electrode kinetics can therefore be attributed to mass transport control of diffusing species to and from the electrode surface.

The apparent behavior of the anodic and cathodic limiting current densities in Fig. 2 can be explained in terms of the reversible nature of the complexation reaction as well as the concentrations of the species involved in this reaction. In the bulk solution, the tribromide species dissociates into Br_2 and Br^- species with a relative increase in concentration of 21.0 and 0.002, respectively, when compared with the initial amounts of these species present in the solution. At low k_f values, the equilibrium for the tribromide dissociation reaction is established rather slowly. Nevertheless, the substantial increase in the concentration of Br_2 results in an enhancement of the cathodic limiting current density. On the other hand, the anodic limiting current density is unchanged because the bulk concentration of Br^- remains essentially constant. As the forward rate constant k_f increases, the backward rate constant increases also (since $k_b = k_f K_{eq}$) and equilibrium for the homogeneous reaction is established much more rapidly. As a result of the depletion of Br_2 in the electrode reaction, the tribromide complex formation reaction shifts in favor of dissociation of Br_3^- leading to increased generation of Br_2 and consequently, to further

Fig. 3. Effect of increasing k_f on Br_2/Br^- electrode kinetics under conditions of low concentration of bromide solutions. $c_{\text{Br}_2} = 7.1 \times 10^{-4}\text{M}$, $c_{\text{Br}^-} = 4.1 \times 10^{-3}\text{M}$, and $c_{\text{Br}_3^-} = 0.00\text{M}$, respectively.



enhancement of the cathodic limiting current density as shown in Fig. 2. On the other hand, for the anodic limiting current, in Fig. 2 as k_f increases the Br_2 formed as a result of the oxidation of Br^- by reaction [1] reacts with unreacted Br^- according to Eq. [2] to further decrease the concentration of Br^- at the electrode while at the same time, the concentration of Br_3^- in the vicinity of the electrode is enhanced. This process of Br_3^- complex formation continues until the Br^- concentration in the diffusion layer decreases to a minimum at around $k_f = 10^2 \text{ cm}^6/\text{mol/s}$; this point corresponds to the depression in the anodic limiting current density. Beyond this point, the equilibrium is shifted in favor of the dissociation of Br_3^- , leading to an increase in the concentrations of Br_2 and Br^- in the diffusion layer. As a result, the anodic limiting current shows a gradual rise with increase in k_f until it approaches the value obtained in the absence of tribromide reaction at very high k_f .

In Fig. 3, where low bromine concentrations are used and where initially no tribromide species was present in the solution, at low k_f values ($\leq 10^{-2} \text{ cm}^6/\text{mol/s}$), the cathodic and anodic limiting current densities are less than the case where no complexation occurs in the solution. This indicates that at low k_f values, less Br_2 or Br^- from the bulk solution is available for reaction at the electrode as a result of these species combining to form the tribromide complex. However, as k_f increases ($\geq 10^6 \text{ cm}^6/\text{mol/s}$), the limiting current densities become equal to those obtained in the absence of the complexation reaction, signifying little or no influence of the tribromide

complexation reaction on the electrode kinetics when the homogeneous reaction rate is high.

Efforts to reduce the high activity of Br_2 in Zn/Br_2 batteries during charge (2-4) to improve cell efficiencies make it desirable to study the tribromide complexation reaction, since complexing Br_2 in the form of insoluble or sparingly soluble bromine complexes is a practical way of achieving this goal (2, 16). A change in the bulk concentration of Br_2 or for that matter, of the other active species (Br^- or Br_3^-) will affect the equilibrium of the complexation reaction in Eq. [2] and consequently the electrode kinetics, as indicated by the plots in Fig. 4-6. An increase in the bulk concentration of Br_2 results in an enhancement of the cathodic limiting current density and a decrease in the anodic limiting current density as shown in Fig. 4. The reason for this is that as the bulk concentration of Br_2 is increased, the quantity of Br_2 that is transported to the surface to generate the cathodic current increases too. On the contrary, the increased concentration of Br_2 complexes more of the Br^- in the bulk solution to form Br_3^- species. In this way, the amount of free Br^- species that is transported to the electrode decreases leading to a reduction in the anodic current density. As confirmed in Fig. 4, the higher the concentration of Br_2 in the bulk, the smaller the quantity of Br^- available for reaction at the electrode and the smaller the anodic current density. In a corresponding manner, in Fig. 5, an increase in the bulk concentration of Br^- results in an increase in the anodic current density and a decrease in the cathodic current density.

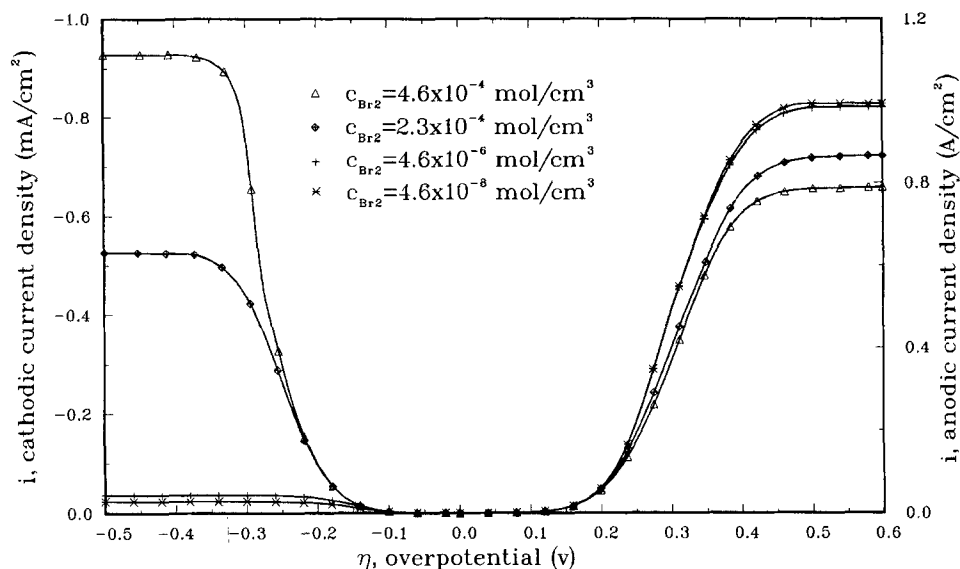


Fig. 4. Effect of a change in Br_2 concentration on the Br_2/Br^- electrode under conditions where Br_3^- is the predominant Br_2 containing species. $c_{\text{Br}^-} = 0.5\text{M}$, $c_{\text{Br}_3^-} = 0.001\text{M}$, $k_f = 10^{12} \text{ cm}^6/\text{mol/s}$.

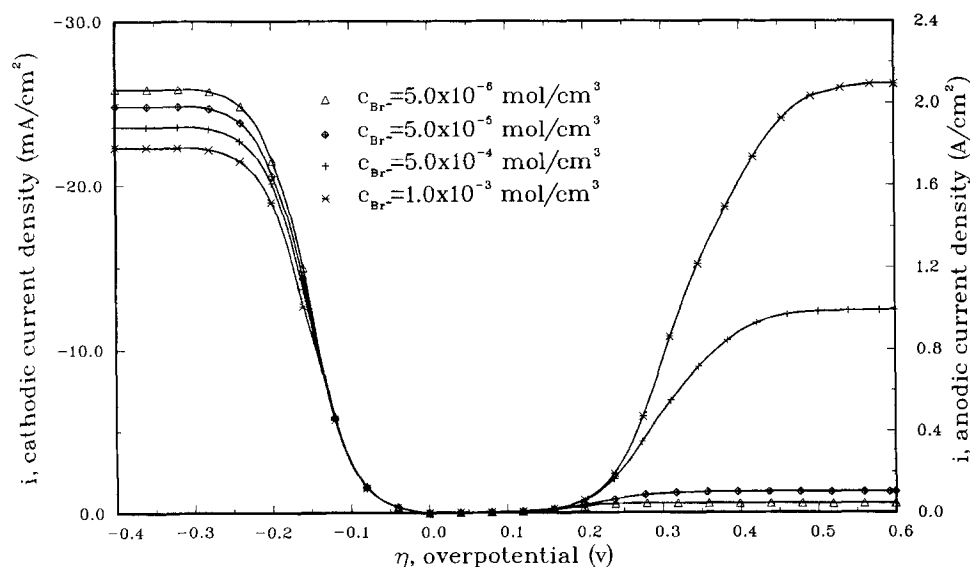


Fig. 5. Effect of a change in Br^- concentration on the Br_2/Br^- electrode under conditions where Br_3^- is the predominant Br_2 containing species. $c_{\text{Br}_2} = 4.6 \times 10^{-2}\text{M}$, $c_{\text{Br}_3^-} = 0.001\text{M}$, $k_f = 10^{12} \text{ cm}^6/\text{mol/s}$.

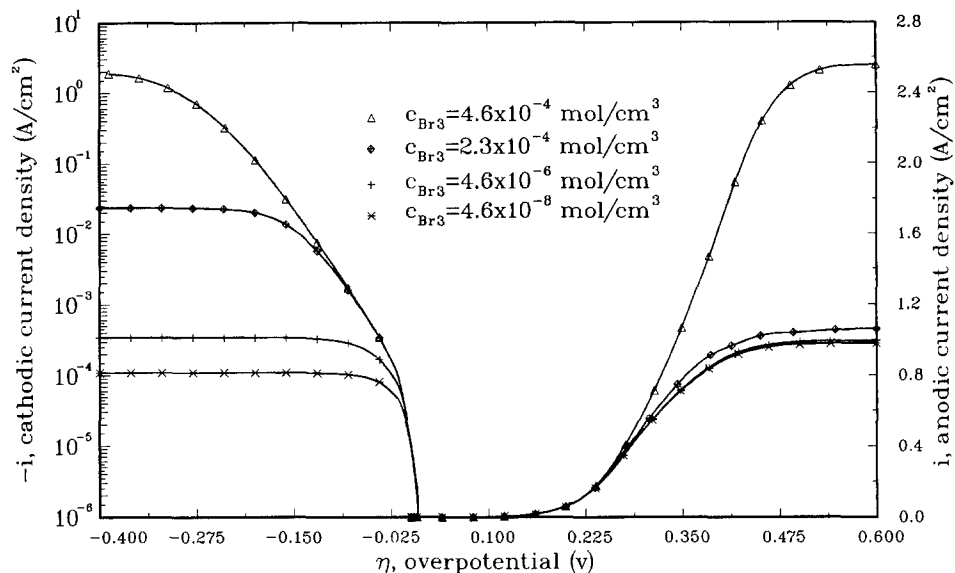


Fig. 6. Effect of a change in Br_3^- concentration on the Br_2/Br^- electrode under conditions where Br_3^- is the predominant Br_2 containing species. $c_{\text{Br}_2} = 4.6 \times 10^{-2} \text{M}$, $c_{\text{Br}^-} = 0.5 \text{M}$, $k_f = 10^{12} \text{cm}^6/\text{mol}\cdot\text{s}$.

Figure 6 demonstrates the predicted effect of a hypothetical change in the bulk concentration of Br_3^- species on the oxidation/reduction current density of Br_2/Br^- electrode under normal operating cell conditions. The anodic and cathodic limiting current densities shown in Fig. 6 are higher at higher concentrations of tribromide in the bulk. As pointed out by Iwasita and Giordano (15) and Mastragostino and Gramellini (5), the Br_3^- does not participate directly in the reaction at the electrode but rather via the formation of Br_2 and Br^- in reaction [2] with which the Br_3^- is in rapid equilibrium. Therefore, an increase in the bulk concentration of Br_3^- shifts the equilibrium in the direction favoring the production of Br_2 and Br^- . This process leads to an increase in the concentration of these species in the bulk solution, and consequently in the amount of these species transported to the electrode as well. The result is an enhancement of both the anodic and cathodic current densities. However, because of the high concentration of Br^- already present in the bulk solution, the additional Br^- generated as a result of the equilibrium dissociation of Br_3^- by reaction [2] is quite small (less than 1%) so that the relative enhancement of the anodic limiting current is far less than that of the cathodic limiting current.

These results are significant particularly, when viewed with respect to the complexation of bromine species into sparingly soluble or insoluble bromine complexes. During charge, in the bromine half-cell of a typical Zn/ Br_2 battery, Br^- is oxidized to Br_2 which then reacts with Br^- in the solution according to Eq. [2] to form Br_3^- . In the presence of a complexing agent such as a quaternary ammonium salt (2), insoluble or sparingly soluble bromine complexes are formed. Formation of these complexes reduces the concentration of Br_2 and Br_3^- in the bulk solution and, as demonstrated in Fig. 4-6, causes a lowering of the oxidation current over the current that would prevail in the absence of the complexation reaction. Conversely, during discharge, the bromine released by the insoluble complex is reduced at the electrode where it enhances the reduction current.

Summary

The influence of the complexation reaction on the current/potential curves is greater at higher homogeneous kinetic rate constants for the Br_2/Br^- electrode with high bromine concentrations. On the other hand, for a Br_2/Br^- electrode with low bromine concentrations and with no initial amount of Br_3^- in the solution, the complexation reaction has practically no effect on the electrode kinetics at higher homogeneous kinetics.

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LIST OF SYMBOLS

c_i	concentration of species i , mol/cm ³
i	current density, A/cm ²
i_0	exchange current density, A/cm ²
k_b	backward rate constant, cm ³ /s
k_f	forward rate constant, cm ⁶ /mol-s
K_{eq}	equilibrium constant, cm ³ /mol
$K'(\zeta)$	pseudo-equilibrium constant at distance ζ from electrode, cm ³ /mol

Greek

$\alpha_{c,v}$	cathodic transfer coefficient for Volmer step
$\alpha_{c,H}$	cathodic transfer coefficient for Heyrovsky step
δ_D	diffusion layer thickness, cm
η	overpotential, corrected for ohmic drop in the solution, when measured with respect to a reference electrode of a given kind, V
μ_c	reaction layer thickness, cm
ν	kinematic viscosity, cm ² /s
ζ	distance from electrode surface relative to the diffusion layer thickness
Ω	rotation speed, rad/s

Subscripts

ref	reference conditions
∞	in the bulk solution

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