Electrode Kinetics of Organodisulfide Cathodes for Storage Batteries

Meilin Liu,* Steven J. Visco,* and Lutgard C. De Jonghe
Department of Materials Science and Engineering, University of California, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

ABSTRACT

The electrode kinetics of a diverse group of organodisulfide cathode materials have been systematically investigated. The electrochemical behavior of these redox couples was studied as a function of the organic moiety (R) in the organodisulfide compounds (RSSR). These studies were performed with a variety of working electrodes, including platinum, glassy carbon, graphite, stainless steel, aluminum, and copper. The possible reaction pathways and mechanisms have been hypothetically postulated, theoretically analyzed, and experimentally verified. Observations showed that while electron transfer rate constants varied with organic moiety, the mechanistic details of the redox path were invariant with the R groups of the organodisulfides studied. The reaction mechanism, as determined from experimental observations, can be expressed as

\[ 2[RS' \rightarrow RS' + e^{-}] \]

\[ RS' + RS' \rightarrow RSSR \]

for the oxidation of thiolate anions (RS-) to the corresponding organodisulfides. The first step in the redox mechanism, charge transfer, is rate determining, while the second step, chemical reaction, is at equilibrium. The observed transfer coefficients are quite asymmetric and vary as a function of the R group in RSSR and the electrode materials. The standard rate constants are also affected by the nature of the organic moiety, R, and are in the range of 10^-8-10^-6 from ambient to 100°C. Further, and in particular, electrode kinetics have been enhanced by the addition of several electrocatalysts.

Advanced high temperature secondary batteries incorporating solid electrolyte separators offer many advantages over conventional cells, including high specific energy and power density, as well as excellent charge retention on storage due to negligible self-discharge. Still, the impressive performance of these cells is offset somewhat by the technical difficulties of operating batteries at high temperatures. Accordingly, various efforts have been made to introduce alternative high specific power/energy batteries operating at reduced temperatures (1-4), including the sodium/β-alumina/RSSR cell (5). However, since mass transport and electrode kinetics are thermally activated, a thorough understanding of these processes is necessary for successful operation of lower temperature systems.

It is well known that the efficiency and power of an electrochemical energy conversion system increases with increasing the rate of electrode kinetics and mass transport, and with decreasing internal resistance. Accordingly, for batteries such as the alkali metal/organodisulfide cells (6), the critical limitations on charge-transfer rates are essentially determined by the nature of the positive electrode. Although the electrode reactions of organodisulfide/thiolate redox couples have been reported previously to be kinetically kindered (6, 7), particularly at ambient temperatures, their reversibility can be substantially enhanced by introducing appropriate electrocatalysts. The identification of effective catalysts, however, can only emerge from a detailed understanding of the kinetic mechanisms that control the overall process.

The investigation of electron transfer reaction kinetics generally involves the determination of reaction rate, mechanism, and kinetic parameters (8). The reaction route refers to a successive sequence of elementary reactions which constitute the overall, stoichiometric electrode reaction, while the mechanism specifies the rate-controlling nature of the constituent steps and their coupling (9). The basic kinetic parameters characterizing an electrode reaction include: (i) the reaction order, (ii) the standard rate constant or exchange current density, (iii) the symmetry factor for the rate determining step (rds) or apparent transfer coefficients, (iv) the stoichiometric coefficients, and (v) the activation energy. The above parameters can be determined from the dependence of reaction rate (i.e., current) on various observables, including overpotential across the interface, composition of the electrolytic solution adjacent to the electrode, the nature of the electrode surface, and temperature.

The purpose of this study is to elucidate the kinetic behavior of a diverse group of organodisulfide/thiolate redox couples, and to provide a basis for identifying effective electrocatalysts for activation of these redox reactions. The effect of temperature on electrode kinetics as well as on transport properties will be addressed in a subsequent communication (10).

Experimental

Organosulfur compounds (tetramethylthiuram disulfide (TMTD), tetraethylthiuram disulfide (TETD), phenyl disulfide (PDS), di-fluorophenyl disulfide (FPDS), sodium di-ethyl dithiocarbamate (NaEDC), sodium dimethyl dithiocarbamate (NaDMDC), tetramethylammonium perchlorate (TEAP), dimethylsulfoxide (DMSO), phenyl disulphide (PDS), dimethyl disulfide (TMTD), tetraethylthiuram disulfide (TETD), tetraethylthiuram disulfide (TEAP), reference electrode filling electrolyte [tetramethylammonium chloride (TMAC)], methyldisulfide (DMDS) was obtained from Aldrich 1 and distilled under vacuum over molecular sieves. Transition metal phthalocyanines (MPc), were obtained from Pfaltz & Bauer 2 and stored in an argon atmosphere dry box.

An Ag/AgCl reference electrode 3 was connected to the working electrode compartment with a Luggin capillary salt bridge containing a 0.1M TEAP solution. The reference electrode compartment contained a 0.1M TMAC aqueous solution saturated with AgCl.

Three-electrode electrode electroanalytical cells with platinum auxiliary electrodes were used throughout the experiments. Planar disks (diam = 0.8 cm) of platinum, glassy carbon, graphite, stainless steel, aluminum, and copper metal were used as the working electrodes. Before each experiment, the working electrodes were polished to a mirror finish with diamond paste (1 μm) and rinsed with acetone.

Unless otherwise stated, electrolyte solutions consisted of 0.1M TEAP in DMSO and electrolyte potentials were measured vs. a Ag/AgCl reference electrode. The electrolyte solutions were purged with dry argon for about 10 min prior to experimentation and continuously purged at slower rates during each measurement.

1 Aldrich Chemical Company, Incorporated, Milwaukee, Wisconsin 53233.
3 Astra Scientific.

1 Present address: Ceramatec, Incorporated, Salt Lake City, Utah 84119.

* Electrochemical Society Active Member.
In rotating disk voltammetry (11-13), linear or triangular potential functions, generated by a PAR 173 potentiostat/galvanostat4 in conjunction with a PAR 175 Universal Programmer,4 were applied to a disk electrode immersed in the electrolyte solution (150 cm³). The rotation speed of the disk electrode was modulated with an ASR Electrode Rotator5 and Speed Controller. The corresponding current response was either recorded with a 4120T Bascom-Turner digital recorder6 or acquired with an IBM-PC/AT computer through a DT2801A data translation board7 using ASYSTANT® software. The potential sweep rates ranged from 1 to 10 mV/s.

Solution viscosities were measured using a series of Cannon-Fenske Routine Viscometers immersed in an isothermal water bath. The measurement involved determination of the time required for a given volume of the solution to fall through a vertical capillary tube of a given length under the influence of gravity. The apparatus constant of each viscometer was determined through calibration with distilled water.

In linear and Tafel polarization measurements the potential was stepped by a PAR 173 potentiostat/galvanostat4 and the corresponding currents at each potential were recorded using a Bascom-Turner recorder. Complications due to mass transfer were eliminated by either stirring the electrolyte solution with a magnetic bar when a stationary electrode was used, or by measuring the current at a RDE at high rotation speed (about 3000 rpm).

Sodium/β'-alumina/RSRR cells were galvanostatically controlled by an IBM-PC/AT computer through a DT2801A data translation board1 and a PAR 173 potentiostat/galvanostat4 using a program written in ASYST,8 while the corresponding cell voltages were simultaneously acquired by the computer.

1 Princeton Applied Research, Hayward, California 94545.
2 Pine Instrument Company, Grove City, Pennsylvania 16127.
3 Bascom-Turner, Incorporated, Norwood, Massachusetts 02062.
4 Data Translation, Incorporated, Marlborough, Massachusetts 01752-1192.
5 Macmillan Software Company.

**Kinetic Equations (14-18)**

It was determined previously that the overall, stoichiometric reaction for organodisulfide/thiolate redox couples can be described as (6)

$$RSSR + 2e^- \rightleftharpoons 2RS^-$$

[1]

Under the assumption that complications due to electrode adsorption are negligible, the relationship between current, i, and overpotential at the electrode surface, η, can be described by (14, 16)

$$i = \frac{\alpha_i}{\eta^\alpha} F^\eta \left[ \exp \left( \frac{\alpha_i F\eta}{RT} \right) - \exp \left( \frac{\alpha_i F\eta}{RT} \right) \right]$$

[2]

where \(i_0\) is the exchange current, \(\eta_{RS^-}\) and \(\eta_{RSSR}\) are the anodic and cathodic reaction orders for species RS⁻ and RSSR, and \(C_{RS^-}\) and \(C_{RSSR}\) are the concentrations of species i at the electrode surface and in the bulk solution, respectively. The anodic and cathodic transfer coefficients, \(\alpha_a\) and \(\alpha_c\), can be expressed as (16)

$$\alpha_a = \frac{\gamma}{\nu} + \tau(1 - \alpha)$$

[3a]

$$\alpha_c = \frac{\gamma}{\nu} + \tau\beta$$

[3b]

where \(\gamma\) is the number of electrons transferred in the steps preceding the rds, \(\gamma\) is the number of electrons transferred in the steps after the rds, \(\tau\) is the number of electrons transferred in the rds, \(\nu\) is the stoichiometric coefficient, and \(\beta\) is the symmetry factor of the rds.

The exchange current can, in general, be expressed as (15)

$$i_0 = \frac{(n/v)FA\kappa\theta(C_{RSSR})}{(C_{RS^-})^{\gamma}(C_{RSSR})^{\gamma\theta}}$$

[4]

where \(n\) is the total number of electrons involved in the overall reaction, \(\kappa\) is the standard rate constant, and the exponents \(\mu\) and \(\lambda\) are constant dependent on the reaction mechanism.

**Table 1. Possible reaction pathways and the corresponding mechanisms for organodisulfide/thiolate redox couples**

<table>
<thead>
<tr>
<th>Reaction route</th>
<th>rds</th>
<th>Mechanism no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. EC route</td>
<td>2RS⁻ = \frac{k_a}{k_c} RS⁺ + e⁻ ]</td>
<td>(1-1)</td>
</tr>
<tr>
<td></td>
<td>2RS⁻ = \frac{k_2}{k_1} RSSR ]</td>
<td>(1-2)</td>
</tr>
<tr>
<td>2. ECE route</td>
<td>RS = \frac{k_1}{k_2} RS⁺ + e⁻ ]</td>
<td>(2-1)</td>
</tr>
<tr>
<td></td>
<td>RS⁻ + RS = \frac{k_2}{k_1} RSSR ]</td>
<td>(2-2)</td>
</tr>
<tr>
<td></td>
<td>RSSR = \frac{k_2}{k_1} RSSR + e⁻ ]</td>
<td>(2-3)</td>
</tr>
<tr>
<td>3. CEE route</td>
<td>2RS⁻ = \frac{k_1}{k_2} RSSR ]</td>
<td>(3-1)</td>
</tr>
<tr>
<td></td>
<td>RSSR = \frac{k_2}{k_1} RSSR + e⁻ ]</td>
<td>(3-2)</td>
</tr>
<tr>
<td></td>
<td>RSSR = \frac{k_2}{k_1} RSSR + e⁻ ]</td>
<td>(3-3)</td>
</tr>
<tr>
<td>4. EEC route</td>
<td>RS = \frac{k_1}{k_2} RS⁺ + e⁻ ]</td>
<td>(4-1)</td>
</tr>
<tr>
<td></td>
<td>RS = \frac{k_2}{k_1} RS⁺ + e⁻ ]</td>
<td>(4-2)</td>
</tr>
<tr>
<td></td>
<td>RS⁻ + RS = \frac{k_2}{k_1} RSSR ]</td>
<td>(4-3)</td>
</tr>
</tbody>
</table>
Table II. Kinetic equations and the corresponding reaction orders, transfer coefficients, and stoichiometric coefficients for nine possible reaction mechanisms listed in Table I

<table>
<thead>
<tr>
<th>Mechanism no.</th>
<th>Overall reaction rate (mol cm⁻² s⁻¹)</th>
<th>Reaction order</th>
<th>Transfer coefficient</th>
<th>Stoichiometric coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( r_1 = k_{ad}(C_{RS^-}) \exp \left( \frac{(1 - \beta_1)FE}{RT} \right) - k_{b} C_{RSSR} \exp \left( -\frac{\beta_1 FE}{RT} \right) )</td>
<td>1</td>
<td>( \frac{1}{2} )</td>
<td>1 - ( \beta_1 ), ( \beta_1 )</td>
</tr>
<tr>
<td>2</td>
<td>( r_2 = k_{ad} \frac{k_{a}}{k_{a}^2} (C_{RS^-})^2 \exp \left( \frac{2FE}{RT} \right) - k_{b} C_{RSSR} )</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>( r_1 = k_{ad}(C_{RS^-}) \exp \left( \frac{(1 - \beta_2)FE}{RT} \right) - k_{d} k_{ad} (C_{RSSR}) \exp \left( -\frac{ FE}{RT} \right) )</td>
<td>1</td>
<td>1</td>
<td>1 - ( \beta_2 ), ( 1 + \beta_2 )</td>
</tr>
<tr>
<td>4</td>
<td>( r_2 = k_{a} \frac{k_{d}}{k_{d}^2} (C_{RS^-})^2 \exp \left( \frac{ FE}{RT} \right) - k_{d} C_{RSSR} \exp \left( -\frac{ FE}{RT} \right) )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>( r_3 = k_{a} \frac{k_{d}}{k_{d}^2} (C_{RS^-})^2 \exp \left( \frac{(2 - \beta_3)FE}{RT} \right) - k_{d} (C_{RSSR}) \exp \left( -\frac{ FE}{RT} \right) )</td>
<td>2</td>
<td>1</td>
<td>2 - ( \beta_3 ), ( \beta_3 )</td>
</tr>
<tr>
<td>6</td>
<td>( r_1 = k_{d} C_{RS^-} \exp \left( \frac{FE}{RT} \right) - k_{ad} k_{d} ) ( C_{RSSR} ) \exp \left( -\frac{ FE}{RT} \right) )</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>( r_2 = k_{a} \frac{k_{d}}{k_{d}^2} (C_{RS^-})^2 \exp \left( \frac{(1 - \beta_2)FE}{RT} \right) - k_{d} (C_{RSSR}) \exp \left( -\frac{ FE}{RT} \right) )</td>
<td>2</td>
<td>1</td>
<td>1 - ( \beta_2 ), ( 1 + \beta_2 )</td>
</tr>
<tr>
<td>8</td>
<td>( r_2 = k_{a} \frac{k_{d}}{k_{d}^2} (C_{RS^-})^2 \exp \left( \frac{(2 - \beta_3)FE}{RT} \right) - k_{d} ) ( C_{RSSR} ) \exp \left( -\frac{ FE}{RT} \right) )</td>
<td>1</td>
<td>1</td>
<td>2 - ( \beta_2 ), ( \beta_2 )</td>
</tr>
<tr>
<td>9</td>
<td>( r_3 = k_{a} \frac{k_{d}}{k_{d}^2} (C_{RS^-})^2 \exp \left( \frac{2FE}{RT} \right) - k_{d} C_{RSSR} )</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

\( \nu_{RS^-} = \left( \frac{\partial \ln (i_R)}{\partial \ln (C_{RS^-})} \right)_{C_{RSSR}} \) \( \nu_{RSSR} = \left( \frac{\partial \ln (i_R)}{\partial \ln (C_{RSSR})} \right)_{C_{RSSR}} \)

Mechanistic Analysis (15, 16)

Listed in Table I are a number of possible reaction pathways considered in the analysis, EC, ECE, CEE, and EEC routes, together with the corresponding reaction mechanisms. The kinetic parameters associated with each mechanism, such as reaction orders, transfer coefficients, and dependence of exchange current densities on concentration, can be derived as follows.

First, assume the reaction takes the EC route (see Table I). Then, the reaction rate for each elementary step can be expressed as (15)

\( r_1 = i_F = k_{ad} C_{RS^-} \exp \left[ (1 - \beta_1)\frac{FE}{RT} \right] - k_{b} C_{RSSR} \exp \left[ -\beta_1 \frac{FE}{RT} \right] \) \[6a\]

\( r_2 = k_{b} \frac{C_{RS^-}^2}{k_{b}^2} - k_{b} C_{RSSR} \) \[6b\]

Depending on the rate-controlling nature of each step, two possible reaction mechanisms result.

1. The first step, charge transfer, is the rate-determining step (rds) and the second step, chemical reaction, is at equilibrium. In this case, the concentration of the radical RS⁻ is given by

\( C_{RS^-} = (k_{b}/k_{a} C_{RSSR})^{1/2} \) \[7\] and

\( r_1 = i_F = k_{ad} C_{RS^-} \exp \left[ \alpha \frac{FE}{RT} \right] - k_{b} (k_{a}/k_{ad} C_{RSSR})^{1/2} \exp \left[ -\alpha \frac{FE}{RT} \right] \) \[8a\]

or

\( i = i_{0} \exp \left( \frac{(C_{RS^-} - C_{RS^-})}{C_{RSSR}} \right) \exp \left[ \alpha \frac{FE}{RT} \right] - (C_{RSSR}/C_{RSSR})^{1/2} \exp \left[ -\alpha \frac{FE}{RT} \right] \) \[8b\]

where

\( i_{0} = F A k_{a} \exp \left( \frac{(C_{RS^-} - C_{RS^-})}{C_{RSSR}} \right) \exp \left[ \alpha \frac{FE}{RT} \right] \) \[9\]

indicating that \( \mu = \alpha \kappa \) and \( \lambda = \alpha_{2} \kappa \). The standard rate constant can be expressed by the rate constants associated with each elementary step as

\( k_0 = k_{ad} \kappa^{1/2} \kappa_{a}^{1/2} \) \[10\]

In this case, the reaction order for species RS⁻ and RSSR are 1 and 1/2, respectively. The transfer coefficients are related to the symmetry factor as

\( \alpha_{c} = \beta_1 \) \[11a\]

\( \alpha_{a} = 1 - \beta_1 \) \[11b\]

2. If the chemical reaction is the rds and the charge-transfer step is at equilibrium, then the overall reaction rate can be expressed as

\( i = i_{0} \exp \left[ 2 \alpha \frac{FE}{RT} \right] - (C_{RSSR}/C_{RSSR})^{1/2} \exp \left[ -\alpha \frac{FE}{RT} \right] \) \[12\]

where

\( i_{0} = 2F A k_{a} \kappa C_{RSSR} \) \[13\]

and the overall reaction rate can be expressed as

\( k_0 = k_{b} \) \[14\]
Table III. Dependence of exchange currents on concentrations of organodisulfide/thiolate salt for the possible reaction mechanisms listed in Table I

<table>
<thead>
<tr>
<th>Mechanism no.</th>
<th>Exchange current</th>
<th>$\mu$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$i_0 = AFk^c(C_{RSS})^\alpha(C_{RSSS})^{1/2 - \beta}$</td>
<td>$\beta_1$</td>
<td>$1 - \beta_1/2$</td>
</tr>
<tr>
<td>2</td>
<td>$i_0 = 2AFk^cC_{RSS}$</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>$i_0 = 2AFk^c(C_{RSS})^\alpha(C_{RSSS})^{1/2 - \beta}$</td>
<td>$\beta_1$</td>
<td>$1 - \beta_1/2$</td>
</tr>
<tr>
<td>4</td>
<td>$i_0 = 2AFk^cC_{RSS} - (C_{RSS})^{1/2}$</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>5</td>
<td>$i_0 = 2AFk^c(C_{RSS})^\alpha(C_{RSSS})^{1/2 - \beta}$</td>
<td>$\beta_1$</td>
<td>$1 - \beta_1/2$</td>
</tr>
<tr>
<td>6</td>
<td>$i_0 = 2AFk^cC_{RSS}$</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>$i_0 = 2AFk^c(C_{RSS})^{1/2} - (C_{RSSS})^{1/2}$</td>
<td>$(1 + \beta)$</td>
<td>$1 - \beta_1/2$</td>
</tr>
<tr>
<td>8</td>
<td>$i_0 = 2AFk^cC_{RSS} - (C_{RSSS})^{1/2}$</td>
<td>$(\beta_2 - 1)$</td>
<td>$1 - \beta_2/2$</td>
</tr>
<tr>
<td>9</td>
<td>$i = 2AFk^cC_{RSS}$</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

In this case, the reaction order for species $RS$ is 2 and that for species $RSSR$ is 1. The corresponding anodic and cathodic transfer coefficients are 2 and 0, respectively, indicating that the reaction rate in the cathodic direction is independent of electrode potential. Further, the exponents for the concentration dependence of exchange currents are 1 for $\mu$ and 0 for $\lambda$, indicating that $i_0$ is independent of the concentration of thiolate anions.

Similar analyses have been performed for other possible reaction pathways, i.e., the ECE, CEE, and EEC routes in Table I.

The governing kinetic equations and the corresponding reaction orders, transfer coefficients, and stoichiometric coefficients for the nine possible reaction mechanisms derived from the above four possible reaction pathways have been tabulated in Table II. The corresponding expression for the exchange current and its dependence on concentration, as defined in Eq. [4], were summarized in Table III for the various reaction mechanisms.

### Electrochemical Methods

**Rotating disk electrode techniques** (19-21).—Reaction orders for various organodisulfides and the corresponding thiolate anions were determined from the dependence of the current at an RDE on rotation speed at constant electrode potential without varying the bulk concentration (since the effective concentration of electroactive species at the surface of an RDE is a function of rotation speed).

The current at an RDE can, in general, be expressed as

$$i = i_0 [1 - c_i/c_{i,b}]$$  \[15a\]

where $i_0$ is the convective-diffusive limiting current given by

$$i_0 = 0.62(\alpha F A/C_{i,b}D_{3/2}v^{-1/2}a^{1/2})$$  \[15b\]

Combining Eq. [2] and [15], one can relate the anodic or cathodic current at an RDE, $i$, to $i_0$ and $i_k$ as

$$i_k = [1 - i/i_0]^{\beta_1}$$  \[16\]

where $i_k$ is the pure kinetic current (as defined in Eq. [5]). At a given potential, the kinetic current is a constant (and can be determined from extrapolation at $\omega \to 0$). The reaction order for species $i$, $\gamma_i$, can be expressed as

$$\gamma_i = \frac{d[\log(i_0)]}{d[\log(1 - i_0/i_{k,b})]}$$  \[17a\]

and

$$\gamma_{RSSR} = \frac{d[\log(i_0)]}{d[\log(1 - i_0/i_{k,b})]}$$  \[17b\]

where $i_0$ (or $i_x$) is the current measured at a given rotation speed and $i_{k,b}$ (or $i_{k,c}$) is the convective-diffusive limiting current at the same rotating speed.

When $\gamma_i = 1$, i.e., the reaction is first order for species $i$, Eq. [16] can be rewritten as

$$1/i = 1/i_0 + 1/i_k$$  \[18\]

Thus, the plot of $1/i$ vs. $\omega^{-1/2}$ at a constant potential is a straight line. The intercepts ($1/i_0$) give an estimate of kinetic current ($i_k$) at a given potential, while the slopes ($d(1/i)/d(\omega^{-1/2})$) allow assessment of the diffusion coefficients.

**Polarization measurement**.—Exchange currents, transfer coefficients, and stoichiometric coefficients were determined from polarization measurements at either stationary electrodes or rotating disk electrodes under experimental constraints that the electrochemical processes were completely controlled by kinetics.

When $|\eta| >> RT/F$, the Tafel approximation of Eq. [5] gives

$$i_a = i_0 \exp (\alpha_F nF/RT)$$  \[19a\]

and

$$i_c = i_0 \exp (-\alpha_F nF/RT)$$  \[19b\]

The exchange currents were obtained directly from the intercepts of the Tafel plots. The anodic and cathodic transfer coefficients were calculated from the Tafel slopes. The stoichiometric coefficients were determined from the transfer coefficients and the total number of electrons involved in the overall reaction as

$$\gamma = n/(\alpha_a + \alpha_c)$$  \[20\]

When $|\eta| << RT/F$, linear approximation of Eq. [5] gives

$$i_a = i_0(\alpha_a + \alpha_c)(F/RT)$$  \[21\]
The slope of the linear plot of \( i \) against \( \eta \) allows determination of the exchange current, \( i_0 \). The standard rate constants were calculated from \( i_0 \) using Eq. [4].

The dependence of the exchange current on concentration was further used to verify the transfer coefficients and the reaction mechanism. The theoretical values of \( \alpha \) and \( \beta \) corresponding to different reaction mechanisms are tabulated in Table III.

### Results and Discussion

**Reaction order (mechanism determination).**—Linear sweep voltammograms at a platinum disk electrode, rotated at different rates, are shown in Fig. 1a for oxidation of the thiolate anion FPT\(^{-}\) to disulfide FPDS. The convective-diffusive limiting currents in the anodic direction, \( i_{\text{a},\text{a}} \), are shown in Fig. 1b for oxidation of various thiolate anions to the corresponding disulfides at a platinum electrode. The bulk concentration of thiolate salt in the electrolyte solution was \( (m) 2.8 \text{ mM NaDEDC}, (c) 2.4 \text{ mM NaDMDC}, (z) 2.2 \text{ mM NaFPT}, \) and \((o) 2.1 \text{ mM NaPT} \). A close to 0.5 indicating that the reduction of RSSR to RS\(^{-}\) is a half-order reaction.

Accordingly, the determination of reaction orders, in this case, uniquely suggests that the electrode reaction takes the EC route with the first step, charge transfer, as the rate-determining step, i.e.

### Table IV. Calculated diffusion coefficients of thiolate anions (from RDE measurements at 293 K)

<table>
<thead>
<tr>
<th>Thiolate anion</th>
<th>( C_n ) (( \mu \text{mol cm}^{-2} ))</th>
<th>Viscosity (( \text{cm}^2 \text{s}^{-1} ))</th>
<th>Diffusion coefficient (( 10^{-9} \text{ cm}^2 \text{s}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDC(^{-})</td>
<td>2.8</td>
<td>0.02178</td>
<td>3.13 ± 0.58</td>
</tr>
<tr>
<td>DMDC(^{-})</td>
<td>2.4</td>
<td>0.02185</td>
<td>3.17 ± 0.21</td>
</tr>
<tr>
<td>FPT(^{-})</td>
<td>2.2</td>
<td>0.02183</td>
<td>1.46 ± 0.10</td>
</tr>
<tr>
<td>FT(^{-})</td>
<td>2.1</td>
<td>0.02214</td>
<td>0.67 ± 0.06</td>
</tr>
</tbody>
</table>

### Table V. Observed reaction orders and anodic transfer coefficients for organodisulfide/thiolate redox couples at platinum electrode (determined from RDE measurements at 293 K)

<table>
<thead>
<tr>
<th>RSSR/RS(^{-})</th>
<th>Reaction order</th>
<th>Transfer coefficient ( \alpha_\text{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TETD/DEDC(^{-})</td>
<td>0.95 ± 0.05</td>
<td>0.49 ± 0.01</td>
</tr>
<tr>
<td>TMTD/DMDC(^{-})</td>
<td>0.87 ± 0.06</td>
<td>0.49 ± 0.03</td>
</tr>
<tr>
<td>FPDS/FPT(^{-})</td>
<td>0.80 ± 0.03</td>
<td>0.51 ± 0.02</td>
</tr>
<tr>
<td>PDS/FT(^{-})</td>
<td>0.90 ± 0.04</td>
<td>0.53 ± 0.03</td>
</tr>
</tbody>
</table>
Transfer coefficient, rate constant, and stoichiometric coefficients.—Shown in Fig. 3b are the Tafel plots constructed from the kinetic currents \( i_{k} \) obtained at \( \omega \to \infty \) for oxidation of RS\(^{-} \) to RSSR. The kinetic currents in the anodic direction, \( i_{k,a} \), were determined from the intercepts with the \( i^{-1} \) axis in the reciprocal Levich plot (i.e., \( i^{-1} \) vs. \( \omega^{-1/2} \)) as shown in Fig. 3a. The anodic transfer coefficients, calculated from the Tafel slopes are listed in Table V. Since the reduction of RSSR to RS\(^{-} \) is a half-order reaction, the plot of \( i^{-1} \) vs. \( \omega^{-1/2} \) for reduction is not a straight line (Eq. [18] is not valid) and hence the kinetic current in the cathodic direction, \( i_{k,c} \), cannot be extrapolated from a plot similar to those for the anodic kinetic current. Instead, the cathodic kinetic currents were approximated by the currents directly measured at an RDE while increasing the rotation speed up to 3000 rpm; at low overpotentials \( i_{k,c} \) is well below \( i_{k,a} \) so that the approximation is adequate.

Shown in Fig. 4a are the currents directly measured at a platinum RDE for various organodisulfide/thiolate redox couples. The deviation from linear Tafel behavior observed at high overpotentials was brought about by mass-transfer limitations. At these potentials, electrode kinetics were sufficiently rapid so that mass transport of the electroactive species to and from the electrode surface was unable to maintain the surface concentration close to the bulk concentration. Still, there does exist a sufficiently wide potential range over which Tafel behavior prevails and the Tafel slopes are well defined. The transfer coefficients and stoichiometric coefficients calculated from these Tafel slopes within this range and the standard rate constants estimated from the intercepts are tabulated in Table VI for different RSSR/RS\(^{-} \) couples.

The experimentally determined transfer coefficients and stoichiometric coefficients further confirm that the electrode reaction is correctly described by Eq. [22] (mechanism 1).

Concentration dependence.—Polarization measurements were also performed on electrolyte solutions having various concentrations of organodisulfides and their corresponding thiolate salts. Cell currents between a platinum disk working electrode and a platinum counterelectrode were measured at rotation speed of 3000 rpm. The exchange currents were then determined from the intercepts of the corresponding Tafel plots and the slopes of the linear polarization plots.

Figure 5a shows the dependence of \( i_{k} \) on \( C_{RS^{-}} \) for various redox couples at a constant bulk concentration of organodisulfide. The slopes of the plots, \( d \log \left( i_{k} \right) / d \log (C_{RS^{-}}) \), directly yield the kinetic parameter \( \mu \). Figure 5b shows the dependence of \( i_{k} \) on \( C_{RSSR} \) at a constant concentration of the corresponding thiolate salt. The slopes of these plots, \( d \log (i_{k})/d \log (C_{RSSR}) \), allows estimation of the kinetic parameter \( \lambda \). Deviations from linearity indicate that the
parameters; these values are probably more valuable in predicting actual device behavior than parameters based on absolute surface areas.

Thus, the electroactive surface area of the electrode might face area of the electrode and therefore are apparent parameters. Nevertheless, the average values, as listed in Table VII, agree reasonably well with the transfer coefficients as determined from the Tafel slopes. Also, the observed exponents closely match the theoretical values for mechanism 1 (Table III), supplying further evidence for the validity of this mechanism.

Electrode materials.—Tafel plots for various redox couples at a glassy carbon RDE are shown in Fig. 4b. The experimental conditions were identical to those for the measurements at a platinum electrode as shown in Fig. 4a. The estimated transfer coefficients, stoichiometric coefficients, and standard rate constants are summarized in Table VIII. Comparison with the behavior observed at platinum electrodes, allows several conclusions: (i) for the redox couples TETD/DEDC− and TMTD/DMDC−, the equilibrium potentials established at a glassy carbon electrode (Eoe) were shifted in the positive direction with respect to those at a platinum electrode, indicating that stronger adsorption of the thiolyte anions occurs on graphite than on platinum; (ii) for FPDS/FPT− and PDS/PT−, however, the equilibrium potentials were shifted in the negative direction, indicating that stronger adsorption of these organodisulfides takes place on glassy carbon than on platinum; (iii) the exchange current densities at glassy carbon electrodes are higher than those at platinum electrodes, and are modified somewhat by the R group in the RSSR molecule.

Although all working electrodes were polished to a mirror finish before each run, it is conceivable that some electrodes might have partially passivated or adsorbed chemical species upon immersion into the electrolyte solutions. Thus, the electroactive surface area of the electrode might be different from its geometric surface area. Throughout this study, the surface area dependant parameters determined at each electrode were based on the geometric surface area of the electrode and therefore are apparent parameters; these values are probably more valuable in predicting actual device behavior than parameters based on absolute surface areas.

Table VII. Dependence of exchange currents at platinum electrode on concentrations of organodisulfides/thiolate salts (determined from polarization measurements at 293 K)

<table>
<thead>
<tr>
<th>RSSR/RS−</th>
<th>Exponents</th>
<th>λ</th>
<th>μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TETD/DEDC−</td>
<td>0.33 ± 0.02</td>
<td>0.34 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>TMTD/DMDC−</td>
<td>0.32 ± 0.03</td>
<td>0.37 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>FPDS/FPT</td>
<td>0.24 ± 0.03</td>
<td>0.52 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>PDS/PT</td>
<td>0.23 ± 0.04</td>
<td>0.94 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

Tafel plots for TETD/DEDC− at platinum, graphite, and glassy carbon electrodes are compared in Fig. 6a. An immediate observation is that the exchange current densities or rate constants at graphite electrodes are about an order of magnitude higher than that at platinum electrodes. This is in agreement with a previous cyclic voltammetry study (6), where the separations of peak potentials at graphite electrodes were much smaller than at platinum electrodes. Also, the shift of the equilibrium potential from −0.280V at a platinum electrode to −0.187V at a glassy carbon electrode can be explained by stronger adsorption of thiolyte anions at graphite or glassy carbon relative to platinum (6). Further, the measured transfer coefficients at platinum electrodes were slightly more symmetric than those at glassy carbon electrodes. In addition, the apparent exchange current densities at graphite electrodes are much higher (more than three times) than those at glassy carbon electrodes. This may be partially explained as being due to a slightly rougher surface of the graphite electrode than that of the glassy carbon electrode. However, since both electrodes were carefully polished before experimentation (hence the difference in their surface areas cannot fully account for the large difference in their apparent exchange current densities), it is likely that the chemical nature of the surfaces exerts a strong effect on electrode kinetics.
Fig. 7. Polarization behavior of Na/beta-alumina/RSSR cells (cell capacity: 2000C) with dimethylsilisulfide (DMDS) cathodes (at 378 K): (a) applied sequential transient current pulses, (b) the corresponding cell potential response, and (c) cell polarization obtained from pulse polarization measurements.

Tafel polarization of platinum, graphite, and stainless steel electrodes in concentrated RSSR/RS- solutions at 373 K are shown in Fig. 6b. The cell currents were measured at stationary electrodes while the electrolyte solution was vigorously stirred by a magnetic spin bar. The potential range over which Tafel polarization was observed was narrow, and deviations at high overpotentials were probably brought about by insufficient mass transport. Nevertheless, in conjunction with the determination of exchange current densities from the slopes of the corresponding linear polarization plots (i.e., \( \eta \) when \( \eta < 0 \)), the Tafel slopes were determined without ambiguity. The estimated transfer coefficients and the standard rate constants for different electrode materials, averaged over values obtained at different concentrations of TETD and NaDED, are summarized in Table IX.

In addition to inert electrodes such as platinum and carbon, stainless steel, aluminum, and copper electrodes were also investigated. Stainless steel electrodes were found to passivate quickly in the electrolyte solution and subsequently behave like platinum electrodes, but the measured exchange current densities were much lower.

Upon immersion of an aluminum electrode in an electrolyte solution containing 1.34M TETD and 1.34M NaDED in DMSO at 373 K, an initial corrosion potential of -1.6V was observed, which decayed to approximately -0.36V in about 3 min, and then remained relatively stable. The exchange current at a passivated aluminum electrode was

Table VIII. Observed transfer coefficients, stoichiometric coefficients, and standard rate constants for organodisulfide/thiolate redox couples at glassy carbon electrodes (determined from polarization measurements at 293 K)

<table>
<thead>
<tr>
<th>RSSR/RS- Concentration (( \mu \text{mol cm}^{-2} ))</th>
<th>Equilibrium potential ( E_{eq}(V) )</th>
<th>Transfer coefficient ( \alpha_a )</th>
<th>Stoichiometric coefficient ( v )</th>
<th>Standard rate constant ( k \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TETD/DEDC- 2.1 2.2</td>
<td>-0.187 ± 0.013 0.69 ± 0.007 0.31 ± 0.006 2 ± 0.013 0.69 ± 0.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMTD/DMDC -0.133 ± 0.011 0.63 ± 0.012 0.27 ± 0.007 2 ± 0.021 1.0 ± 0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FPDS/FPT -0.441 ± 0.009 0.35 ± 0.011 0.67 ± 0.019 2 ± 0.051 2.3 ± 0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDS/PT -0.523 ± 0.012 0.47 ± 0.013 0.59 ± 0.016 2 ± 0.065 1.62 ± 0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table IX. Observed transfer coefficients and standard rate constants for TETD/DEDC- at different electrode materials

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Transfer coefficient</th>
<th>Standard rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_a )</td>
<td>( \alpha_c )</td>
<td>( k \times 10^6 (293 K) )</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.65 ± 0.009</td>
<td>0.35 ± 0.008</td>
</tr>
<tr>
<td>Glassy carbon</td>
<td>0.67 ± 0.015</td>
<td>0.33 ± 0.013</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.67 ± 0.021</td>
<td>0.33 ± 0.023</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>0.64 ± 0.021</td>
<td>0.36 ± 0.018</td>
</tr>
</tbody>
</table>
about an order of magnitude lower than that at a passivated stainless steel electrode. Unlike aluminum which passivated slowly, copper electrodes were actively corroded in the electrolyte solution. As soon as a copper electrode was immersed in the electrolyte solution, the portion of the solution adjacent to the electrode surface turned jet black (the color of the copper complex CuDDC) and the corrosion potential shifted continuously in the positive direction as more copper was corroded.

Electrocatalysis.—The polarization behavior of a Naβ⁺-alumina/RSSR cell with a dimethyldisulfide (DMDS) positive electrode, with and without cobalt phthalocyanine (CoPc) as an electrocatalyst, is shown in Fig. 7. Sequential transient current pulses applied to the cells are shown in Fig. 7a and the corresponding cell potential responses are shown in Fig. 7b. Clearly, the cell polarization was dramatically reduced by introducing CoPc, as shown in Fig. 7c. The discharge of these cells (Fig. 8) further demonstrates that the performance of the Na/RSSR cell with CoPc was greatly improved relative to the cell without CoPc. In fact, the reduction of Na/RSSR cell overpotential by phthalocyanine addition was observed on both charge and discharge, indicating that electrocatalysis is probably due to adsorbed phthalocyanine on the graphite felt current collector. Other transition metal phthalocyanines and transition metal thiolate species, including Co, Fe, Cu, Zn, Ti, etc., were also found to have some catalytic effect. The electrocatalysis of RSSR/R⁺ redox couples by adsorbed transition metal phthalocyanines has been reported previously for the related cystine/cysteine redox couple (22). The use of adsorbed phthalocyanines to enhance the activity of the graphite electrode is analogous to the use of modified electrodes for similar purposes (23, 24). However, further studies are needed to elucidate the detailed catalytic mechanism.

Conclusions

The observed reaction orders for the RSSR/R⁺ redox couples are 1 in the anodic direction and 1/2 in the cathodic direction. The determined transfer coefficients are β and (1 − β) for the cathodic and anodic process, respectively; this indicates that the rate-determining step is repeated twice (ν = 2) for the completion of the overall reaction. The reaction pathway, therefore, takes the EC route (Table I) with the first step, charge transfer, as the rate-determining step. The kinetics of the electrode reaction, then, are fully described by Eq. [6][11].

The transfer coefficients and the standard rate constants for various redox couples at different electrode materials as well as at different temperatures are summarized in Tables V and X.

Electrocatalysts, such as transition metal phthalocyanines and transition metal thiolate slates have been successfully utilized to assist charge transfer.

The high apparent exchange current densities at graphite electrodes suggested that graphite is a good positive electrode material, while the stability of stainless steel and aluminum metals towards the RSSR/R⁺ electrolyte solutions makes them likely candidates for cell case materials.

Acknowledgments

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LIST OF SYMBOLS

Abbreviations

DDEC — diethyl dithiocarbamate anion,
[(CH3)2NCSS]–

DMDC — dimethyl dithiocarbamate anion,
[(CH3)2NCSS]–

DMDS — dimethyldisulfide, [CH3–S–CH3]–

DMSO — dimethylsulfoxide

FPDS — di-fluorophenyl disulfide, (F-C6H4–S–)2

FPT — fluorophenyl thiolate anion, (F–C6H4–S)–

MPC — metal phthalocyanine

NaDDEC — sodium diethyl dithiocarbamate,
(CH3)2NCSS-Na

NaDMDC — sodium dimethyl dithiocarbamate,
(CH3)2NCSS-Na

NaFPT — sodium fluorophenyl thiolate, F–C6H4-S-Na

NaPT — sodium phenyl thiolate, C6H5–S-Na

PDS — phenyl disulfide, (C6H5–S–)2

Pt — thiolate anion, [C6H5–S]–

R — an organic moiety

RDE — rotating disk electrode

rds — rate-determining step

RPM — rotation per minute

RS — a group of thiolate ions

RSSR — a group of organic disulfides

TEAP — tetraethylammonium perchlorate,
(CH3)4NClO4

TFTD — tetrafluorothiuram disulfide, ((C2H5)2NCSS)–

TMAC — tetramethylammonium chloride, (CH3)4NCl

TMTD — tetramethylthiuram disulfide, ((CH3)2NCSS)–

Notation

A — electrode area, cm²

C_i — concentration of species i (i = RS⁻ or RSSR), μmol cm⁻²

C_i,es — concentration of species i at electrode surface, μmol cm⁻²

C_i,° — concentration of species i in the bulk solution, μmol cm⁻²

D_i — diffusion coefficient of species i, cm² s⁻¹

E — equilibrium potential of an electrode vs. a reference, V

E° — equilibrium potential of an electrode vs. a reference, V

F — Faraday’s constant, 96,487 C equiv.⁻¹

i — pure kinetic current as defined by Eq. 5, μA

i_k — pure kinetic current in anodic and cathodic direction, μA

i limiting current, μA

i_i,α, β, γ, δ, τ, θ, ξ — limiting current in anodic and cathodic direction, μA

k_i, α, β, γ, δ, τ, θ, ξ — exchange current, μA

k — standard rate constant, (mol/s-cm²)(cm²/s)(mol⁻α)⁻¹

k_no, k_β — rate constants in anodic and cathodic direction for elementary step i (i = 1, 2, 3)

k α, β, γ, δ, τ, θ, ξ — rate constants in forward and backward direction for a chemical reaction

n — number of electrons transferred in the overall reaction (n = α + γ + τ + θ + ξ)

r — number of electrons transferred in the rds

R — universal gas constant, 8.3143 [J mol⁻¹ K⁻¹]

T — absolute temperature, K

Greek

ω — transfer coefficients (as defined in Eq. [2] or [5])
Homogeneous and Heterogeneous Catalytic Reactions in Cobalt Oxide/Graphite Air Electrodes

I. Chemical Kinetics of Peroxide Decomposition by Co(II) Ions in Alkaline Solutions

S. P. Jiang, Z. G. Lin, and A. C. C. Tseung

Chemical Energy Research Center, The City University, Northampton Square, London EC1V OHH, England

ABSTRACT

This paper considers the role played by dissolved cobaltous ions in concentrated alkaline solutions in the homogeneous decomposition of \( \text{H}_2\text{O}_2 \) and its significance to oxygen reduction in alkaline media. Dissolved cobaltous ions, in the form of \( \text{HCoO}_2^- \) in concentrated alkaline solutions, show a very high catalytic activity for the decomposition of \( \text{H}_2\text{O}_2 \) even at a concentration of 1 ppm. The homogeneous decomposition of peroxide is not a simple first-order reaction as reported in literature but is a 1.2 order reaction. It is suggested that kinetics of decomposition of \( \text{H}_2\text{O}_2 \) in the presence of Co\(^{3+} \) ions is controlled by the homogeneous catalytic reaction of the \( \text{HCoO}_2^- \) ions, the heterogeneous redox reaction between \( \text{HCoO}_2^- \) ions in solution, and the Co\(^{3+} \) ions in the cobalt oxide spinel lattice sites.

Oxygen reduction on carbon, graphite, and certain metal oxides in alkaline solutions is considered to proceed through the formation of peroxide intermediate

\[
\text{O}_2 + \text{H}_2\text{O} + 2e^- = \text{HO}_2^- + \text{OH}^- \quad [1]
\]

with the standard potential of \(-0.0649\text{V}\) (vs. SHE at 25°C) (1). The electroreduction of \( \text{H}_2\text{O}_2 \) is unlikely to occur at normal operating potential, and further reaction would involve the decomposition of \( \text{HO}_2^- \) if \( \text{HO}_2^- \)-decomposing catalysts are present

\[
2\text{HO}_2^- = 2\text{OH}^- + \text{O}_2 \quad [2]
\]

The released oxygen is then further reduced, leading to higher efficiency and open-circuit voltage (2). The kinetics and mechanisms of such oxygen reduction reactions have been extensively studied on various transition metal oxide/carbon or graphite electrodes. All the previous studies proposed that the peroxide intermediate is heterogeneous decomposed on the active surface sites of transition metal oxides, and the reaction was considered to be first-order (3-5).

However, it is well-known from Pourbaix diagram (6) that in alkaline solutions, cobalt oxides have a tendency to dissolve gradually in the potential range for oxygen reduction. In concentrated alkaline solution (ca. \( \text{pH} > 10.6 \)), the dissolved cobaltous ion \( \text{Co}^{2+} \) is in the form of the dicobaltite ion \( \text{HCoO}_4^- \), which is characterized by blue color (7)

\[
\text{Co}^{2+} + 2\text{H}_2\text{O} = \text{HCoO}_4^- + 3\text{H}^+ \quad [3]
\]

Efremov et al. (8) have shown that contact between \( \text{CoO}_4 \) and KOH solution leads to changes in the spinel structure, forming simple cobalt oxides, \( \text{CoO} \) and \( \text{Co}_2\text{O}_3 \). Cyclic vol-