Introduction of Kinetics of Electrode Processes

2019 -2020 Academic Year, Fall semester

Sep. 19, 2019
0. Brief introduction

0.0 Course information

http://course.sdu.edu.cn/G2S/Template/View.aspx?action=view&courseType=1&courseId=244&ZZWLOOKINGFOR=G
0. Brief introduction

0.0 Course information

Prof. Shu-Yong ZHANG 张树永

Ph. D. in Physical Chemistry;
Professor in chemistry;
Supervisor for Ph. D in Electrochemistry;

(1) Corrosion and protection of metal: organic coating, conversion layer, surface modification;
(2) Power sources: lithium-ion battery, fuel cell: direct/indirect formate-formic acid fuel cell;
(3) Electrochemical preparation: electrosynthesis, electroarchitecting;
(4) Electroanalysis: electrochemical sensors, modification electrodes.
0.0 Course information

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0. Brief introduction

0.1 Processes occurring on electrode surface

\[ \text{[Fe(CN)\textsubscript{6}]\textsuperscript{3-} + 1e^- \rightarrow [Fe(CN)\textsubscript{6}]\textsuperscript{4-}} \]

- Diffusion
- Chemical conversion
- Adsorption/desorption
- Electrochemical reaction
- Adsorption/desorption
- Chemical conversion
- Diffusion
0. Brief introduction

0.1 Processes occurring on electrode surface

**Electrode process:** The overall changes occurring at or near an electrode surface during the passage of current.

**Electrochemical step:** involving gain or loss of electron: electrochemical oxidation/reduction;

**Non-electrochemical step:** without gain or loss of electron: mass transport (diffusion, convection, migration), adsorption-desorption, chemical conversion (no redox reaction).

**Electrochemical thermodynamics:** reversible/theoretical process

**Electrochemical kinetics:** irreversible/real process
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0.2 Review of fundamental electrochemistry

(1) Electrochemical apparatus:

- Galvanic/Voltaic cell
- Electrolytic cell
- Electrodes: positive/negative electrode, anode / cathode
- Anodic/cathodic region/compartment
- Electrolyte solution?
- Second-type conductor?
0. Brief introduction

0.2 Review of fundamental electrochemistry

(1) Electrochemical apparatus:

working electrode (W. E.)

counter electrode (auxiliary electrode) (C. E.)

reference electrode (R. E.)

Luggin capillary
0.2 Review of fundamental electrochemistry

(2) Types of working electrodes

1) metal / metal ion electrode
2) metal / insoluble salt electrode
3) redox electrode
4) membrane electrode
5) intercalation electrode
6) modification electrode
7) semiconductor electrode
8) insulator electrode
0. Brief introduction

0.2 Review of fundamental electrochemistry

(2) Types of working electrodes

- disk
- sphere
- wire
- ring
- band
- foil
- array
- Interdigitated array

(2) The requirements of counter electrode
0. Brief introduction

0.2 Review of fundamental electrochemistry

(2) Reference electrodes

Commercial Ag/AgCl or Ag/Ag⁺ electrode

Commercial SCE
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0.2 Review of fundamental electrochemistry

(2) Reference electrodes
## 0.2 Review of fundamental electrochemistry

### (4) Kind of electrode reactions

| Direct          | Reaction of electrode | 1) Active Dissolution  
2) Surface finishing  
3) Passivation  
4) Surface conversion  
5) Anodization |
|-----------------|-----------------------|------------------------|
| Indirect via electron media | Reaction of species from solution | 1) Oxidation / Reduction  
2) Polymerization  
3) deposition/crystalization |
| Direct          | Reaction of species in solution | 1) Oxidation via Ce$^{4+}$  
2) Reduction via V$^{2+}$  
3) Polymerization  
4) deposition |

**Direct and indirect electrochemical reactions**
0.3 Important relationships

(1) Faraday’s Law

\[ m = \frac{Q}{zF} M \]

\( m \), mass of liberated matter; \( Q \) electric coulomb, \( z \) electrochemical equivalence, \( F \) Faraday’s constant, \( M \) molar weight of the matter.

\[ F = 1.6021917 \times 10^{-19} \text{ C} \times 6.022169 \times 10^{23} \text{ mol}^{-1} \]

\[ = 96486.69 \text{ C mol}^{-1} \]

\[ \approx 96500 \text{ C mol}^{-1} \]
0.3 Important relationships

(2) Nernst equation:

\[
E = E^{\Theta} - \frac{RT}{nF} \ln \frac{a_{C}^c a_{D}^d}{a_{A}^a a_{B}^b}
\]

\[
\varphi = \varphi^{\Theta} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}
\]

\[
\varphi = \varphi^{\Theta} - \frac{RT}{nF} \ln \prod_{i} a_{i}^{v_i}
\]

Dependent of electrode potential on species activities

Valid only for reversible cell or for electrode at electrochemical reversibility.
0.3 Important relationships

(3) Tafel equation:

\[ \eta = a + b \log j \]

The point of intersection of the extrapolation on the line \( \eta = 0 \) is \( \log i_0 \).

A is in fact the \( \eta \) at \( j = 1 \text{ A cm}^{-2} \).
0.4 Physical meanings of $\phi$ and $I$

(1) Electrode potential

![Graph showing electrode potential and reduction reactions]

Discharge series:

Pt electrode in aq. 0.01 M Fe$^{3+}$, Sn$^{4+}$, Ni$^{2+}$ (1 M HCl)

As potential moved to more negative values, the substance which will be reduced first is the oxidant with the least negative $\phi$. 
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0.4 Physical meanings of $\varphi$ and $I$

(1) Electrode potential

Fermi-Dirac distribution

\[ F(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1} \]

- $E - E_F \gg kT$  
  \[ F(E) = \exp\left(-\frac{E - E_F}{kT}\right) \]

- $E - E_F \ll kT$  
  \[ F(E) = 1 \]

\[ \bar{E} = E_F \]  
\[ F(E) = \frac{1}{2} \]

Fermi Level

\[ E_F = \frac{\hbar^2}{2m_e} \left(\frac{3n_{e^-}}{8\pi}\right)^{2/3} \]

the highest occupied level

\(\text{cf. p. 16-18}\)
0.4 Physical meanings of $\varphi$ and $I$

(1) Electrode potential

- Electrode potential
- Vacant MO
- Occupied MO

A + e$^- \rightarrow A^-$

$A \rightarrow A^+ + e^-$
0.4 Physical meanings of \( \varphi \) and \( I \)

(1) Electrode potential

HOMO approximately corresponds to \( \varphi^\Theta \) of \( \text{A}/\text{A}^- \)

LUMO approximately corresponds to \( \varphi^\Theta \) of \( \text{A}^+/\text{A} \)

Physical meaning of \( \varphi \)?

The tendency to accept or donate electrons is represented by the sign and absolute value of the standard electrode potentials.

That means: high positive potential values indicate a strong tendency for accepting electrons. A higher positive potential of a given half-cell with respect to another indicates that the former has stronger oxidizing ability than the latter.
0.4 Physical meanings of $\varphi$ and $I$

Comparative Electrochemical Study of Unsubstituted and Substituted Bis(phthalocyaninato) Rare Earth(III) Complexes

Peihua Zhu,^[a] Fanli Lu,^[a] Na Pan,^[a] Dennis P. Arnold,^[a,b] Shuyong Zhang,^[a] and Jianzhuang Jiang^[a,c]

\[
\begin{align*}
\text{[M(Pc)}_2\text{]}^{2+} & \xrightarrow{\text{Oxd}_1} \text{[M(Pc)}_2\text{]}^+ \xrightarrow{\text{Oxd}_4} \text{M(Pc)}_2 \xrightarrow{\text{Red}_1} \text{[M(Pc)}_2\text{]}^- \\
\text{[M(Pc)}_2\text{]}^{-5} & \xrightarrow{\text{Red}_2} \text{[M(Pc)}_2\text{]}^{-4} \xrightarrow{\text{Red}_3} \text{M(Pc)}_2 \xrightarrow{\text{Red}_2} \text{[M(Pc)}_2\text{]}^{-2}
\end{align*}
\]

Scheme 2. The one-electron redox processes of $\text{M(Pc)}_2$
0.4 Physical meanings of $\varphi$ and $I$

Comparative Electrochemical Study of Unsubstituted and Substituted Bis(phthalocyaninato) Rare Earth(III) Complexes

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Scheme 1. Bis(phthalocyaninato) rare earth complexes $R^1 = R^2 = H$, $M(Pc)_2$ (A); $R^1 \neq R^2 = H$, tert-C$_4$H$_9$, $M(TBPc)_2$ (B); $R^1 = R^2 = OC_6H_{14}$, $M(OOPc)_2$ (C)

Figure 5. Frontier orbitals of $M(Pc)_2$
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0.4 Physical meanings of $\varphi$ and $I$

(3) Electrochemical window

Investigating the electrochemical windows of ionic liquids

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Fig. 6. EW of [EMim][TFSI] using GC macro-electrode at sweep rate 100 mV/s and 25 °C.
0.4 Physical meanings of $\varphi$ and $I$

(3) Electrochemical window

<table>
<thead>
<tr>
<th>IL</th>
<th>$E_{CL}$</th>
<th>$E_{AL}$</th>
<th>EW</th>
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</thead>
<tbody>
<tr>
<td>[P14,666][TPTP]</td>
<td>−3.64</td>
<td>2.17</td>
<td>5.81</td>
</tr>
<tr>
<td>[N112,102][TFSI]</td>
<td>−3.47</td>
<td>2.52</td>
<td>5.99</td>
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<tr>
<td>[HMPyr][TFSI]</td>
<td>−3.06</td>
<td>2.61</td>
<td>5.67</td>
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<tr>
<td>[BMPyr][TFO]</td>
<td>−2.95</td>
<td>1.88</td>
<td>4.83</td>
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<tr>
<td>[BMPyr][DCA]</td>
<td>−2.95</td>
<td>1.67</td>
<td>4.62</td>
</tr>
<tr>
<td>[BMPyr][TFSI]</td>
<td>−2.92</td>
<td>2.28</td>
<td>5.20</td>
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<tr>
<td>[BMPyr][TFA]</td>
<td>−2.85</td>
<td>1.35</td>
<td>4.20</td>
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<tr>
<td>[EMIm][TFSI]</td>
<td>−2.07</td>
<td>2.12</td>
<td>4.19</td>
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<tr>
<td>[MOEMMor][TPTP]</td>
<td>−1.95</td>
<td>2.03</td>
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<tr>
<td>[MOPMPip][TFSI]</td>
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<td>2.37</td>
<td>4.31</td>
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<tr>
<td>[MOEMMor][TFSI]</td>
<td>−1.93</td>
<td>2.75</td>
<td>4.68</td>
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<tr>
<td>[MOEMPip][TPTP]</td>
<td>−1.75</td>
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<td>3.87</td>
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<tr>
<td>[S222][TFSI]</td>
<td>−1.30</td>
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<tr>
<td>[BMPy][DCA]</td>
<td>−1.25</td>
<td>1.71</td>
<td>2.96</td>
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<tr>
<td>[HPy][TFSI]</td>
<td>−1.22</td>
<td>2.74</td>
<td>3.96</td>
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<tr>
<td>[HPPy][TFSI]</td>
<td>−1.12</td>
<td>2.69</td>
<td>3.81</td>
</tr>
</tbody>
</table>

* The EW of [BMPyr][TFA] was carried out at 35°C as the melting point is 31°C.
Consider 1 mole of $A^{-}$ is oxidized to $A$

$$A^{-} \rightarrow A + ne^{-}$$

$$Q = nNF$$

$n$: the number of $e^{-}$ transferred, $N$ the number of mole of $A$

$$\frac{\partial Q}{\partial t} = I = nF \frac{\partial N}{\partial t} = nFr$$

$$r = \frac{I}{nFA}$$

**Current: the index of reaction rate**
0. Brief introduction

0.4 Physical meanings of $\phi$ and $I$

The power of electrochemical method:
(1) Most powerful oxidation or reduction;
(2) Precise control of reaction rate.
(3) Wide applications.

Humphry Davy

He found element Na and K in 1807 and Ca, Sr, Ba, Mg, in 1808 based on electrolysis.

Henri Moissan

He separated F element from liquid HF containing KHF$_2$ by electrolysis and won 1906 Noble prize.
0.5 Electrochemical methods

One cannot simultaneously control both $E$ and $I$

Control $E$: **potentiostatic methods**

Control $I$: **galvanostatic methods**

Voltammetry -- Voltammetric method
0.5 Electrochemical methods

Steady-state method;
transition method.
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References:


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Vol. 1: Thermodynamics and Electrified Interfaces
Vol. 2: Interfacial Kinetics and Mass Transport
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Vol. 4: Corrosion and Oxide Films
Vol. 5: Electrochemical Engineering
Vol. 6: Semiconductor Electrodes and Photoelectrochemistry
Vol. 7: Inorganic Electrochemistry
Vol. 8: Organic Electrochemistry
Vol. 9: Bioelectrochemistry
Vol. 10: Modified Electrodes
Vol. 11: Index
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Modern Aspects Of Electrochemistry, Vol. 42

1) The electrochemistry and electrocatalysis of Ruthenium in regards to the development of electrodes for Polymer Electrolyte Membrane fuel cells (PEM)
2) Breakthroughs in Solid Oxide Fuel Cell (SOFC) anodes and cathodes leading to improved electrocatalysis
3) Electrocatalysis of the electrochemical reduction of CO$_2$ on numerous metals
4) The interfacial phenomena of electrodeposition and codeposition, and the need for new theoretical analyses of the electrode-electrolyte interface
5) Advantages of scanning tunneling microscopy (STM) in understanding the basics of catalysis, electrocatalysis and electrodeposition
6) The role of electrochemistry in emerging technologies including electrodeposition and electroforming at the micro and nano levels, semiconductor and information storage, including magnetic storage devices, and modern medicine

Vol. 1 Ionics

Vol. 2A Fundamentals of Electrodics

Vol. 2B Electrodics in Chemistry, Engineering, Biology and Environmental Science