

**DEPARTMENT OF INORGANIC  
TECHNOLOGY**

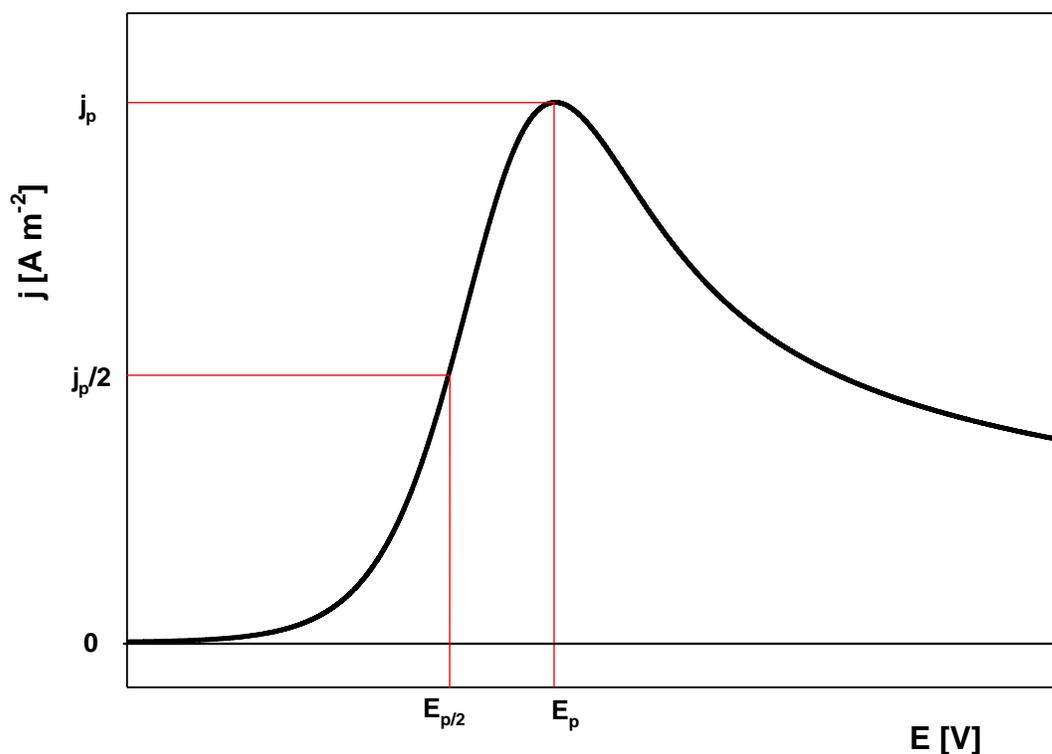
**Technical Electrochemistry, Room No. 23**

**LABORATORY EXERCISE**

**CYCLIC VOLTAMMETRY**

# Cyclic voltammetry

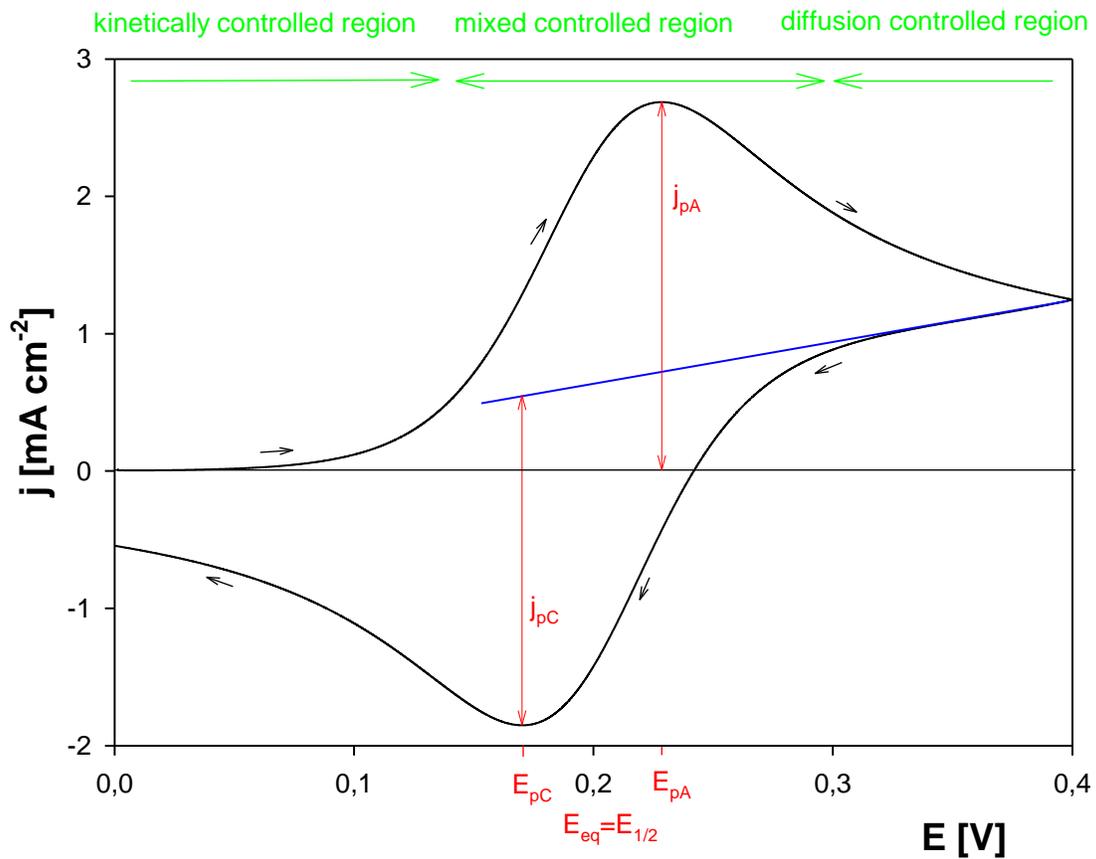
Cyclic voltammetry (CV) belongs to a class of **potentiodynamic** experimental methods. Due to the increasing development of computers and the development of mathematical description of potentiodynamic curves these experimental methods have expanded into the laboratory praxis in the last few decades. Nowadays, it is possible to use these techniques for “routine” determination of studied system characteristics, e.g. kinetic parameters, diffusion coefficient or electrode reaction mechanism.



**Fig. 1:** Potentiodynamic polarization curve.

During CV experiment potential of working electrode is swept linearly from the initial potential  $E_{in}$  to  $E_{max}$  and back to  $E_{in}$ . Thus the basic adjustable parameters are these potential limits  $E_{in}$ ,  $E_{max}$  and potential sweep rate  $v = dE/d\tau$  [ $V s^{-1}$ ]. Other parameters to be controlled are concentration of electroactive species and electrolyte temperature.

In response to applied potential a current starts to flow between the electrodes. Obtained dependence of a current density  $j$  [ $A\ m^{-2}$ ] (current per unit of electrode area) on an electrode potential is called a **polarization curve**. Polarization curve can be thought of as an electrochemical spectrum of a studied system. Generally, each current peak on a polarization curve corresponds to one electrode reaction. Basic peak characteristics are peak potential ( $E_p$ ), peak current density ( $j_p$ ) and potential in the half of the peak ( $E_{p/2}$ ). The way of determination of these values and the value of half-wave potential ( $E_{1/2}$ ) are shown in **Figs. 1 and 2**.



**Fig. 2:** The way of peak current densities and peak potentials determination.

Let's assume reversible electrode reaction:



Each peak can be divided into 3 parts: kinetically controlled, mixed controlled and diffusion controlled region, see **Fig. 2**. The current density in the kinetically controlled region is given purely by the rate of the electron transfer (exponential increase of current density with electrode potential is observed). In mixed controlled region, the transport of electroactive species toward the electrode surface is not fast enough to sustain its constant concentration on the surface. And finally, in diffusion controlled region, the surface concentration of electroactive specie is zero. Thus, rate of reaction (current) is governed purely by diffusion of the electroactive species (current decays linearly with square root of time). Two limiting cases of studied systems can be distinguished - **reversible electrode processes** and **irreversible electrode processes**.

#### *Reversible electrode reactions*

Electrode reaction is said to be reversible if the surface concentrations of electroactive species in kinetically controlled part of polarization curve are given by Nernst equation (**Eq. 2**). This means the rate of the electron transfer is fast enough to sustain equilibrium conditions on the electrode surface during electrode potential sweeping. Typical cyclic voltammogram of reversible electrode process is depicted in **Fig. 2**. Dependence of the electrode potential on time during potentiodynamic experiment can be described by **Eq. 3**. By substituting **Eq. 2** for  $E_\tau$  in **Eq. 3** the dependence of electroactive species concentration ratio on time and potential sweep rate can be expressed (**Eq. 4**).

$$E_\tau = E_{1/2} + \frac{RT}{nF} \ln \frac{c_{o,\tau}}{c_{r,\tau}} \quad (2)$$

$$E_\tau = E_{in} - v\tau \quad (3)$$

$$\frac{c_{o,\tau}}{c_{r,\tau}} = \exp \left[ \frac{nF}{RT} \cdot (E_{in} - v\tau - E_{1/2}) \right] \quad (4)$$

On the basis of these equations the mathematical description of potentiodynamic polarization curve can be derived. This consequently enables one to express the relation for the peak current density (**Eq. 5**). The half peak potential and the difference between the peak potential and the half peak potential are given by **Eqs. 6** and **7**, respectively.

$$j_p^A = 0.4463nFc_o^* \left( \frac{nF}{RT} \right)^{\frac{1}{2}} v^{\frac{1}{2}} D_o^{\frac{1}{2}} \quad j_p^C = 0.4463nFc_o^* \left( \frac{nF}{RT} \right)^{\frac{1}{2}} v^{\frac{1}{2}} D_o^{\frac{1}{2}} \quad (5)$$

$$E_{p/2} = E_{1/2} + 1.09 \cdot \frac{RT}{nF} \quad (6)$$

$$|E_p - E_{p/2}| = 2.2 \cdot \frac{RT}{nF} \quad (7)$$

$$E_p^A - E_p^C = 0.059/n \quad (8)$$

As it can be seen from these relations, the peak potential characteristics are independent of the potential sweep rate in the case of reversible reaction. Another characteristic feature of the reversible reaction is 59 mV difference between anodic and cathodic peak potential is (for n = 1), see **Eq. 8**. The peak current density is however linear function of  $v^{1/2}$ . These expressions can be utilized while determining the number of exchanged electrons or diffusion coefficient of electroactive species.

### ***Irreversible electrode reaction***

Boundary condition at the electrode surface for the totally irreversible electrode reaction is given by electrode reaction kinetics (**Eq. 9**) instead of Nernst equation. Heterogeneous kinetic constant is defined by **Eq. 10**.

$$\frac{j}{nF} = D_o \left[ \frac{dc_{o(x,\tau)}}{dx} \right]_{x=0} = k_{(\tau)} c_{o(0,\tau)} \quad (9)$$

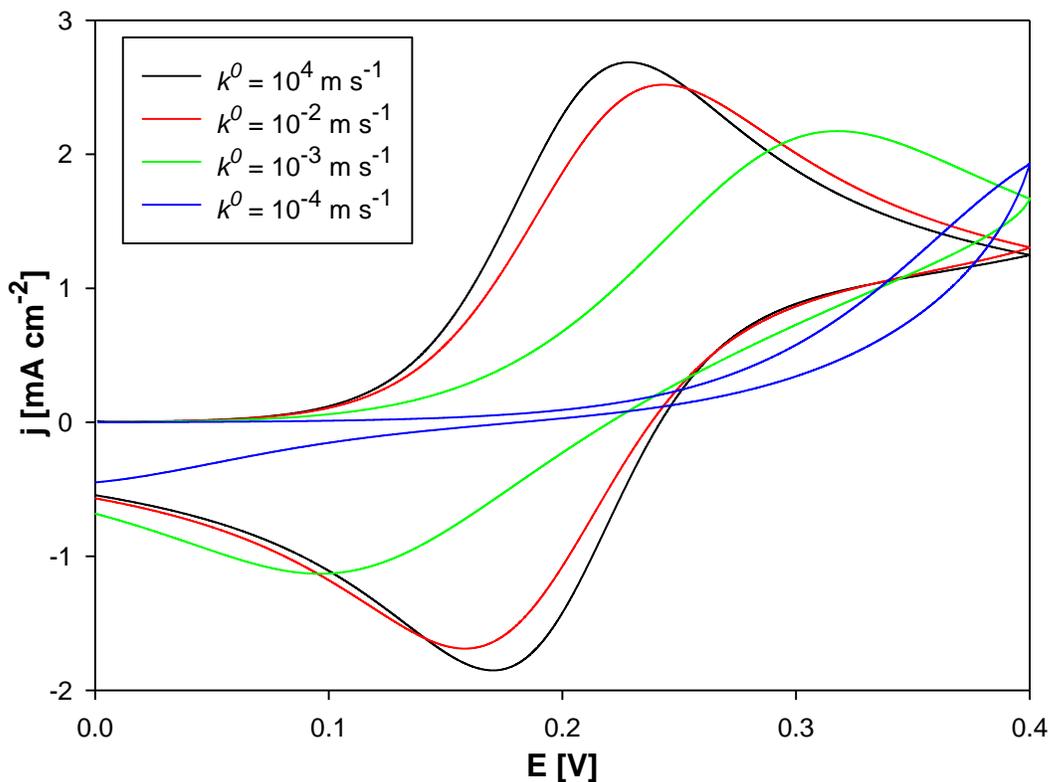
$$k_{(\tau)} = k^0 \cdot \exp \left\{ -\alpha_{A,C} \frac{nF}{RT} [E_\tau - E_{1/2}] \right\} \quad (10)$$

By solving these equations a general form of potentiodynamic polarization curve can be obtained. Consequently the peak current density of irreversible electrode reaction can be expressed by **Eq. 11**. The peak potential and its difference from the half peak potential are given by **Eq. 12** and **13**, respectively.

$$j_p^A = 0.4958nFc_o^* \left( \frac{\alpha_A nF}{RT} \right)^{\frac{1}{2}} D_o^{\frac{1}{2}} v^{\frac{1}{2}} \quad j_p^C = -0.4958nFc_o^* \left( \frac{\alpha_C nF}{RT} \right)^{\frac{1}{2}} D_o^{\frac{1}{2}} v^{\frac{1}{2}} \quad (11)$$

$$E_p^A = konst. + \frac{2.3RT}{2\alpha_A nF} \log v \quad E_p^C = konst. - \frac{2.3RT}{2\alpha_C nF} \log v \quad (12)$$

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha_{A,C}nF} \quad (13)$$



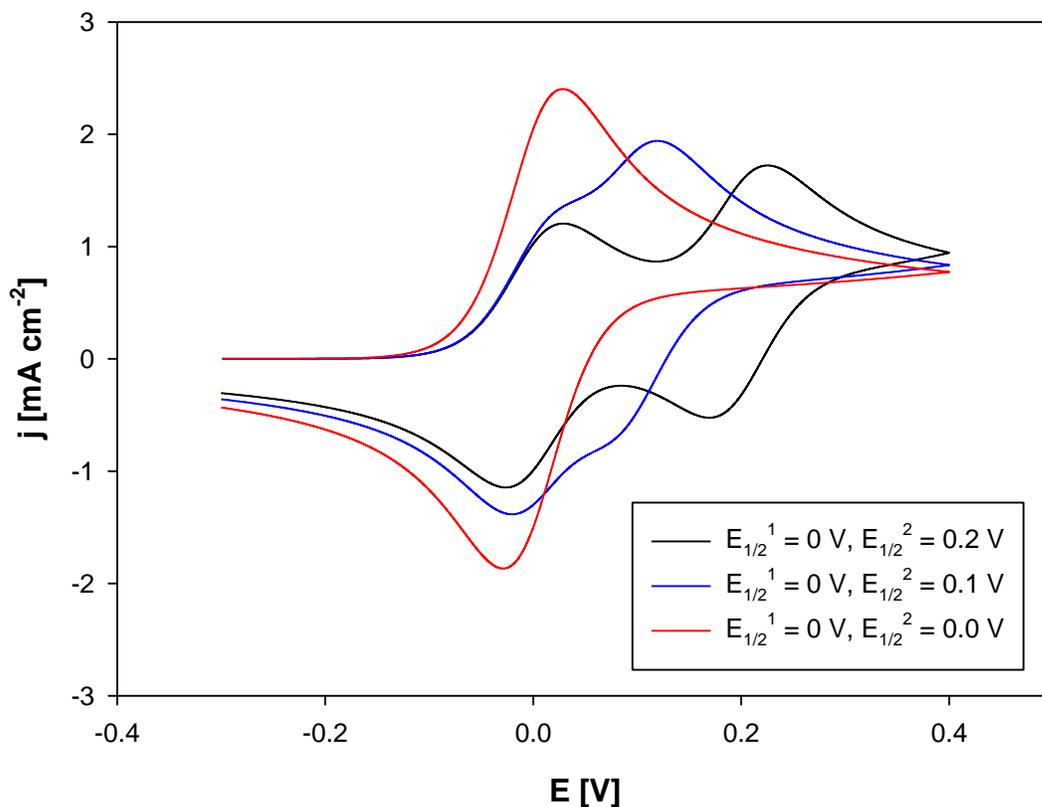
**Fig. 3:** Simulated cyclic voltammograms for reaction  $R \rightleftharpoons O + e$   
 $\nu = 0.02 \text{ V s}^{-1}$ ,  $E_{in} = 0 \text{ V}$ ,  $E_{max} = 0.4 \text{ V}$ ,  $c_R = 10 \text{ mol m}^{-3}$ ,  
 $D_O = D_R = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $E_{1/2} = 0.2 \text{ V}$ ; planar electrode, simulated for  
different  $k^0$  values

It follows from **Eq. 11** that the peak current density of irreversible electrode reaction is also linearly dependent on  $\nu^{1/2}$ , however with different slope. An important difference between reversible and irreversible reactions represents a fact that the peak potential of irreversible electrode reaction is a function of potential sweep rate, particularly  $E_p \sim \log(\nu)$ , see (**Eq. 12**).

#### **Electron transfer rate constant and process reversibility**

Depending on the values of standard heterogeneous rate constant  $k^0$  and potential sweep rate  $\nu$  the process appears to be reversible or irreversible. If  $k^0$  value is sufficiently high a system is able to adapt to the changing electrode potential. Therefore, it is near the state

of equilibrium even at high potential sweep rates  $\nu$ . On the other hand, if  $k^0$  value is low a system is far from the equilibrium even at very low sweep rates  $\nu$ . Cyclic voltammograms in **Fig. 3** corresponds to the electrode reactions with various  $k^0$ , i.e transition of reversible electrode process to irreversible one.



**Fig. 4:** Simulated cyclic voltammograms of 2 independent electrode reactions  $R_1 \rightleftharpoons O_1 + e$ ,  $R_2 \rightleftharpoons O_2 + e$   
 $\nu = 0.02 \text{ V s}^{-1}$ ,  $E_{in} = -0.3 \text{ V}$ ,  $E_{max} = 0.4 \text{ V}$ ,  $c_R = 10 \text{ mol m}^{-3}$ ,  $D_O = D_R = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  
 $k^0 = 10^4 \text{ m s}^{-1}$ , planar electrode,  $E_{1/2}^1 = 0 \text{ V}$ , simulated for different  $E_{1/2}^2$  values

Of course reversible and irreversible systems represent only extreme cases of systems with very fast and very slow reaction kinetics. Systems “in between” that can be classified neither as reversible nor irreversible are called quasireversible. This is, however, out of scope of this text.

Generally spoken, the number of peaks in voltammogram corresponds to the number of electrochemical steps in reaction mechanism. However, as it is shown in **Fig. 4**, all electrode reactions need not necessarily to be visible in the voltammogram. This is the case when half-wave potentials of several processes are close to each other. Then examination of such reactions individually by means of cyclic voltammetry is practically impossible.

## Experimental part

The power of cyclic voltammetry lies in the fact that it enables direct and fast identification of the individual electrode processes. The scope of this work is to determine behaviour of electroactive compound dissolved in the bulk of the electrolyte. Generally spoken, this can be very complex and complicated problem. Aside of electroactive species transport to the electrode surface and its reaction, many other processes can take place. For example preceding or following chemical reaction, adsorption/desorption of reactant, product or intermediate can occur. Moreover, individual processes can take place either in series or in parallel. In the end analysis and interpretation of experimental results in such systems represent significantly complicated problem. As this is an introduction to cyclic voltammetry such complicated systems will be avoided.

### *Determination of electrochemical behavior of KI in aqueous electrolyte.*

#### *Tasks*

1. Prepare 200 ml of KCl solution,  $c_{\text{KCl}} = 0.3 \text{ mol dm}^{-3}$
2. Assemble experimental apparatus and fill the cell with prepared KCl solution
3. Record polarization curve in electrode potential limits from 0 to 1200 mV vs. SCE at electrode potential sweep rate of  $50 \text{ mV s}^{-1}$ .
4. Add KI to KCl solution in such amount to have  $c_{\text{KI}} = 0.01 \text{ mol dm}^{-3}$ .
5. Record polarization curve in electrode potential limits from 0 to 1200 mV vs. SCE at electrode potential sweep rate of  $50 \text{ mV s}^{-1}$ .

Discuss meaning of individual peaks in the measured voltammogram.

6. Perform a series of experiments at  $v = 50 \text{ mV s}^{-1}$ :
  - a. from 0 to 400 mV vs. SCE.
  - b. from 0 to 600 mV vs. SCE.
  - c. from 0 to 800 mV vs. SCE.
  - d. from 0 to 1000 mV vs. SCE.
  - e. from 0 to 1200 mV vs. SCE.

Discuss mutual interconnection of the individual oxidation and reduction peaks.

7. Perform a series of experiments at electrode potentials around the first electrode reaction.
- from 0 to 600 mV vs. SCE,  $5 \text{ mV s}^{-1}$
  - from 0 to 650 mV vs. SCE,  $10 \text{ mV s}^{-1}$
  - from 0 to 700 mV vs. SCE,  $20 \text{ mV s}^{-1}$
  - from 0 to 700 mV vs. SCE,  $50 \text{ mV s}^{-1}$
  - from 0 to 700 mV vs. SCE,  $150 \text{ mV s}^{-1}$
  - from 0 to 700 mV vs. SCE,  $300 \text{ mV s}^{-1}$
  - from 0 to 750 mV vs. SCE,  $500 \text{ mV s}^{-1}$
  - from 0 to 800 mV vs. SCE,  $1000 \text{ mV s}^{-1}$

Evaluate dependence of the peak current density and the peak potential on the potential sweep rate. On the base of results decide on reversibility of the electrode process.

### **Report**

- Plot cyclic voltammograms recorded within tasks 3 and 5 into one graph. Describe individual electrode reactions and possible chemical reactions.
- Plot cyclic voltammograms recorded within tasks 6.a – 6.e into one graph.
- What is relation between a peak current density and the sweep rate? Plot oxidation peak current density (from task 7) as a function of sweep rate.
- What is relation between a peak current density and the sweep rate? Plot the oxidation peak potential (from task 7) as a function of sweep rate.
- Decide whether the oxidation reaction is reversible or irreversible. Give reasons for your decision.
- In the case the reaction is reversible determine diffusion coefficient of I<sup>-</sup> in the electrolyte  $D_{I^-}$ .
  - In the case the reaction is irreversible, determine charge transfer coefficient of oxidation reaction  $\alpha_A$  first. Then determine diffusion coefficient of I<sup>-</sup> in the electrolyte  $D_{I^-}$ .

Note: Description of the plot axes together with stating of proper units is inevitable part of graph ☺.

### List of symbols

$c$	molar concentration	$[\text{mol m}^{-3}]$
$D$	diffusion coefficient	$[\text{m}^2 \text{s}^{-1}]$
$E$	electrode potential	$[\text{V}]$
$j$	current density	$[\text{A m}^{-2}]$
$k$	kinetic constant of electrode reaction	$[\text{m s}^{-1}]$
$n$	number of electrons exchanged during electrode process per molecule of electroactive specie	
$R$	universal gas constant	$[\text{J K}^{-1} \text{mol}^{-1}]$
$T$	thermodynamic temperature	$[\text{K}]$
$v$	electrode potential sweep rate	$[\text{V s}^{-1}]$

### Greek symbols

$\alpha$	charge transfer coefficient	
$\tau$	time	$[\text{s}]$

### Subscripts

$\tau$	function of time
$o$	oxidized compound
$r$	reduced compound
$p$	variable related to the current peak
$x$	function of a distance from the electrode surface
$in$	variable in time $\tau = 0 \text{ s}$
$max$	maximum value of given variable
$A$	variable related to oxidation (anodic) process
$C$	variable related to reduction (cathodic) process

### Superscripts

$A$	variable related to oxidation (anodic) process
$C$	variable related to reduction (cathodic) process
*	concentration in the bulk of electrolyte