

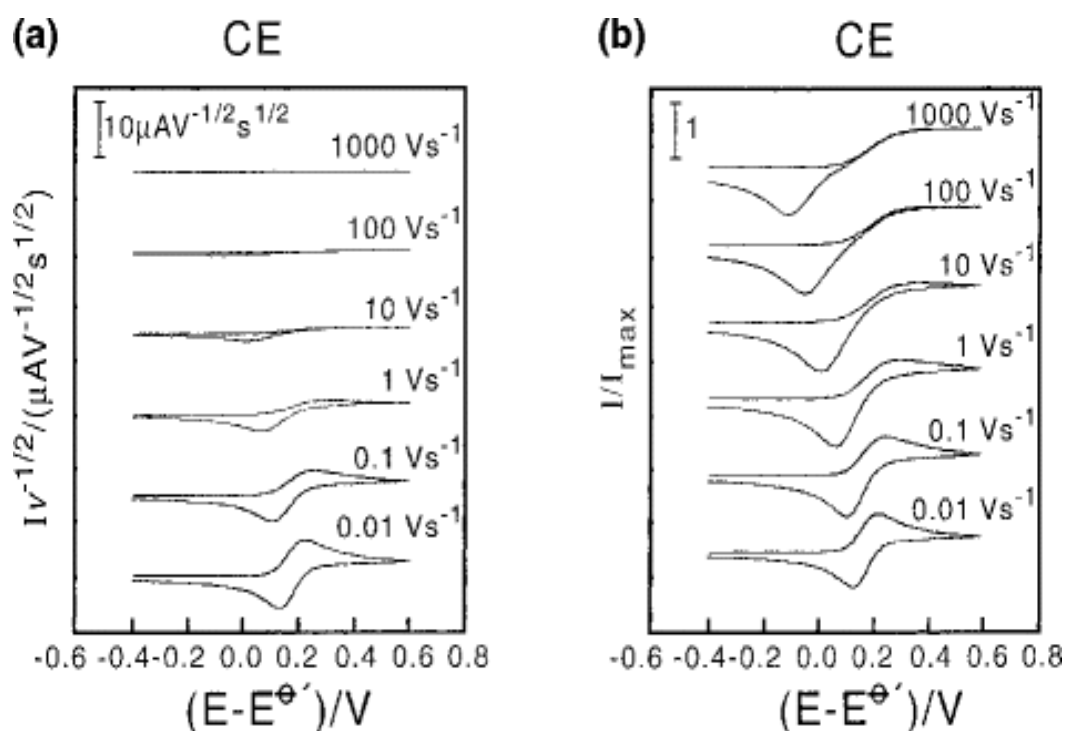
CE Mechanism in Cyclic Voltammetry-Diagnostic Criteria

Rubin Gulaboski

in *Electrochemical Dictionary* (A. J. Bard, G. Inzelt, F. Scholz, 2012)

Abstract


Since the electrochemical transformation of many metal-ligand complexes and various drugs proceeds via a mechanism in which electrochemically active compound is formed via preceding chemical reaction, it is worth to present diagnostic criteria of this important mechanism in cyclic voltammetry. We present set of simulated cyclic voltammograms, and we give practical hints on how to recognize this particular mechanism in cyclic voltammetry. Moreover, we present the readers theoretical methodology relevant to determine kinetics and thermodynamics of chemical step. Model is suitable to get access to the formation (stability constant) of many metal-ligand complexes, but also to get insight into kinetics of many drug-drug interactions. This entry is a part of the *Electrochemical Dictionary* edited by A. J. Bard, G. Inzelt and F. Scholz.

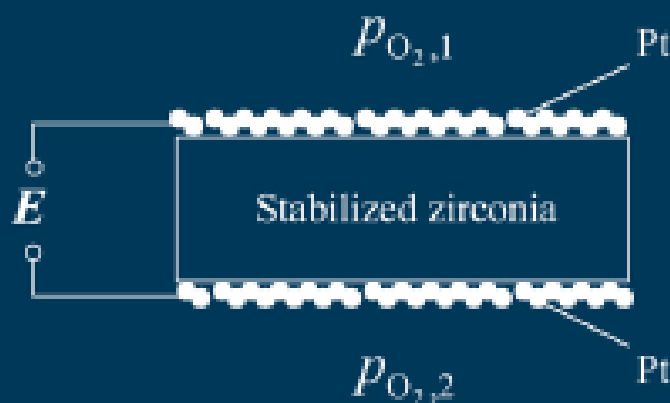


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$$E = E^{\ominus} + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}$$

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Prof. Dr. Allen J. Bard
Hackerman/Welch Regents Chair
Director, Center of Electrochemistry
University of Texas at Austin
Chemistry and Biochemistry
1 University Station A5300
78712 Austin, TX, USA
ajbard@mail.utexas.edu

Prof. Dr. György Inzelt
Eötvös Loránd University
Department of Physical Chemistry
1117 Budapest, Pázmány Péter sétány 1/A, Hungary
inzeltgy@chem.elte.hu

Prof. Dr. Fritz Scholz
University Greifswald
Institute of Biochemistry
Felix-Hausdorf-Straße 4
17487 Greifswald, Germany
fscholz@uni-greifswald.de

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List of Contributors

<p>Prof. Dr. Luisa M. Abrantes Departamento de Química e Bioquímica FCUL Campo Grande 1749-016 Lisboa Portugal luisa.abrantes@fc.ul.pt</p>	<p>LMA</p>	<p>Dr. Friedrich G. K. Baucke Kaiserstr. 36 (505) 55116 Mainz Germany f-baucke@t-online.de</p>	<p>FB</p>
<p>Nir Amir Bar-Ilan University Department of Chemistry 52900 Ramat-Gan Israel niramir75@yahoo.com</p>	<p>NA</p>	<p>Prof. Dr. Johan Bobacka Åbo Akademi University Process Chemistry Centre Laboratory of Analytical Chemistry Biskopsgatan 8 20500, Åbo-Turku Finland johan.bobacka@abo.fi</p>	<p>JB</p>
<p>Prof. Dr. Koichi Aoki Fukui University Department of Applied Physics 9-1, Bunkyo 3-chome Fukui-shi 910 Japan d930099@ipc00.icpc.fukui-u.ac.jp</p>	<p>KA</p>	<p>Prof. Dr. Alan M. Bond Monash University Department of Chemistry Clayton VIC 3168 Australia alan.bond@sci.monash.edu.au</p>	<p>AMB</p>
<p>Prof. Dr. Doron Aurbach Bar-Ilan University Department of Chemistry 52900 Ramat-Gan Israel aurbach@mail.biu.ac.il</p>	<p>DA</p>	<p>PD Dr. Andreas Bund Institut für Physikalische Chemie und Elektrochemie Technische Universität Dresden 01062 Dresden Germany andreas.bund@chemie.tu-dresden.de</p>	<p>AB</p>
<p>Dr. Maximiliano Bárcena Soto Departamento de Química CUCEI Universidad de Guadalajara 44420 Guadalajara, Jalisco Mexico maxbar@gmx.net</p>	<p>MBS</p>	<p>Dr. Orit Chasid Bar-Ilan University Department of Chemistry 52900 Ramat-Gan Israel chasido@mail.biu.ac.il</p>	<p>OC</p>
<p>Prof. Dr. Allen J. Bard Hackerman/Welch Regents Chair Director, Center of Electrochemistry University of Texas at Austin Chemistry and Biochemistry 1 University Station A5300 Austin, TX 78712 USA ajbard@mail.utexas.edu</p>	<p>AJB</p>	<p>Dr. Jorge Correia Departamento de Química e Bioquímica Faculdade de Ciências Universidade de Lisboa Bloco C8, Campo Grande 1749-016 Lisboa Portugal jorge.correia@fc.ul.pt</p>	<p>JC</p>

<p>Dr. Yosef Gofer Bar-Ilan University Department of Chemistry 52900 Ramat-Gan Israel gotfery@mail.biu.ac.il</p>	YG	<p>Dr. Michael Heyrovský Academy of Sciences of the Czech Republic J. Heyrovský Institute of Physical Chemistry Dolejšková 3 182 23 Praha Czech Republic michael.heyrovsky@jh-inst.cas.cz</p>	MHey
<p>Dr. Rubin Gulaboski Universität des Saarlandes Institut für Biophysik Medizinische Fakultät 66421 Homburg Germany rubingulaboski@excite.com</p>	RG	<p>Prof. Dr. Rudolf Holze TU Chemnitz Institut für Chemie, AG Elektrochemie 09107 Chemnitz Germany Rudolf.holze@chemie.tu-chemnitz.de</p>	RH
<p>Prof. Dr. Ulrich Guth Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg Kurt-Schwabe-Straße 4 04720 Ziegra-Knobelsdorf Germany guth@ksi-meinsberg.de</p>	UG	<p>Prof. Dr. György Horányi (†) Institute of Chemistry Chemical Research Center Hungarian Academy of Sciences 1525 Budapest P.O. Box 17 Hungary inzeltgy@chem.elte.hu</p>	GH
<p>Prof. Dr. Andrew Hamnett Principal's Office University of Strathclyde GLASGOW G1 1XQ UK andrewhamnett@mis.strath.ac.uk</p>	AH	<p>Prof. Dr. Ivo A. Hümmelgen Group of Organic Optoelectronic Devices Departamento de Física Universidade Federal do Paraná Caixa Postal 19044 81531-990 Curitiba PR Brazil iah@fisica.ufpr.br</p>	IH
<p>Prof. Dr. Jürgen Heinze Universität Freiburg Institut für Physikalische Chemie Albertstr. 21 a 79104 Freiburg i. Br. Germany juergen.heinze@physchem.uni-freiburg.de</p>	JH	<p>Prof. Dr. György Inzelt Department of Physical Chemistry Eötvös Loránd University 1117 Budapest Pázmány Péter sétány 1/A Hungary inzeltgy@chem.elte.hu</p>	GI
<p>Prof. Dr. Maria Hepel Chemistry Department SUNY Potsdam Potsdam, NY 13676 USA hepelmr@potsdam.edu</p>	MHep	<p>Dr. Heike Kahlert Universität Greifswald Institut für Biochemie Felix-Hausdorff-Str. 4 17487 Greifswald Germany hkahlert@uni-greifswald.de</p>	HK
<p>Dr. Michael Hermes Universität Greifswald Institut für Biochemie Felix-Hausdorff-Str. 4 17487 Greifswald Germany hermesm@uni-greifswald.de</p>	MHer		

CE Mechanism in Cyclic Voltammetry

Rubin Gulaboski RG

By using the \rightarrow formal potential ($E_c^{0'}$) and the \rightarrow standard rate constant (k_s)

$$j_c = -nFk_s c_0(x=0) \exp\left(-\frac{\alpha_c nF(E - E_c^{0'})}{RT}\right), \quad (2)$$

where E is the \rightarrow electrode potential. When $c_0(x=0)$ is substantially higher or lower than c_0^*

$$j_c = -j_0 \frac{c_0(x=0)}{c_0^*} \exp\left(-\frac{\alpha_c nF\eta}{RT}\right). \quad (3)$$

In the potential region of \rightarrow diffusion \rightarrow limiting current ($j_{L,c}$)

$$j_{L,c} = -nFk_{ms} c_0^*, \quad (4)$$

where k_{ms} is the \rightarrow mass transport coefficient.

In the potential region where mixed kinetic-diffusion control prevails

$$j_c = -j_0 (1 - j_c/j_{L,c}) \exp\left(-\frac{\alpha_c nF\eta}{RT}\right). \quad (5)$$

The cathodic partial current may be a sum of several partial currents when two or more electrode processes take place simultaneously (see \rightarrow partial current), e.g., in \rightarrow hydrogen evolution that accompanies metal deposition at high negative potentials.

In this case

$$j_c = j_{1,c} + j_{2,c} \quad (6)$$

$$j_c = -j_{0,1} \frac{c_{0,1}(x=0)}{c_{0,1}^*} \exp\left(-\frac{\alpha_{c,1} n_1 F \eta}{RT}\right) - j_{0,2} \frac{c_{0,2}(x=0)}{c_{0,2}^*} \exp\left(-\frac{\alpha_{c,2} n_2 F \eta}{RT}\right). \quad (7)$$

Refs: [i] Indley-Grüz T, Volmer M (1910) Z. phys. Chem. 4:150-201; [ii] Parsons R (1974) Pure Appl Chem 37:583; [iii] Inzelt G (2002) Kinetics of electrochemical reactions. In: Scholz F (ed) Electroanalytical methods. Springer, Berlin, pp 29-33; [iv] Bard AJ, Faulkner LR (2001) Electrochemical methods. Wiley, New York, pp 98-103

Cathodic stripping voltammetry — Refers to a family of procedures involving a \rightarrow preconcentration by electrochemical oxidation (or reduction) of the analyte (or a salt or derivative of the analyte) onto (or into) the working electrode prior to its direct or indirect determination by means of an electroanalytical technique (see also \rightarrow stripping voltammetry, and \rightarrow anodic stripping voltammetry) [i]. During the stripping step, i.e.,

a voltammetric scan, the deposit is dissolved by **reduction**. A typical example is the oxidative deposition of Hg_2Cl_2 at a \rightarrow mercury electrode from a solution containing chloride ions followed by the **reductive dissolution** of the deposit. Another example is the reductive deposition of Cu_2Se from a Se(IV) solution spiked with Cu^{2+} , and its **reductive dissolution** with formation of copper and H_2Se .

Ref: [i] Fogg AG, Wang J (1999) Pure Appl Chem 71:801

AMB

Catholyte \rightarrow electrolyte solution in the cathodic compartment of an electrolysis cell (see \rightarrow electrochemical cells, \rightarrow electrolyzer) or \rightarrow galvanic cell, i.e., in that part of the cell where the \rightarrow cathode is placed.

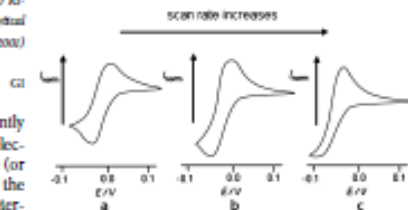
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$C_{\text{rev}}, E_{\text{rev}}$ diagnostics in cyclic voltammetry — Considering the $C_{\text{rev}}, E_{\text{rev}}$ mechanism given with the following reaction scheme for the case of a reduction \rightarrow see process,



the following simple diagnostic criteria apply [1-III]:

- if the chemical step (C) is fast relative to the scan rate, then the cyclic voltammogram shows the features of a simple reversible electron transfer, with a potential shift due to the pre-equilibrium (Fig. 1a) $\rightarrow E_{\text{rev}}$.
- if the chemical step (C) is slow relative to the scan rate, then:



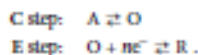
$C_{\text{rev}}, E_{\text{rev}}$ diagnostics in cyclic voltammetry — Figure. The effect of the scan rate on the current components of the simulated cyclic voltammograms of a $C_{\text{rev}}, E_{\text{rev}}$ reaction

- the cathodic current (at more negative potentials) starts to diminish with increasing scan rate (Figs. 1b and c)
- the ratio $I_{p,red}/v^{0.5}$ decreases as the scan rate increases
- the ratio $I_{p,red}/I_{p,ox} < 1$ (for a reduction processes) and it decreases by increasing the scan rate
- in the region of kinetic control, the half-wave peak potential $\Delta E_{p/2}$ (for reduction processes) shifts in negative direction for 30 mV/n per decade increase of the scan rate.

Ref.: [i] Nicholson RS, Shain I (1964) *Anal Chem* 36:706; [ii] Mariken F, Nishideki A, Bond AM (2000) *Cyclic voltammetry*. In: Schultz F (ed) *Electroanalytical methods*. Springer, Berlin, pp 50-97; [iii] Bard AJ, Faulkner L (2000) *Electrochemical methods*. Wiley, New York, pp 471-533

RG

CE process — These are coupled reactions, where the electroactive compound O is produced by a chemical reaction C, which precedes the electron transfer step E:

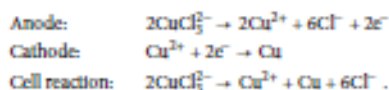


A classical example for a CE process is the reduction of formaldehyde to methanol, where the formaldehyde is formed by dehydration of methan-di-ol [I, II] → chemical reactions in electrochemistry, preceding reaction.

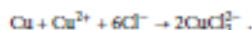
Ref.: [i] Bilewicz R, Wildi K, Osteryoung R, Osteryoung J (1985) *Anal Chem* 62:965; [ii] Bard AJ, Faulkner L (2000) *Electrochemical methods*. Wiley, New York, pp 471-533

RG

CEER process — (Capenhurst electrolytic etchant regeneration process) Electrochemical process for continuous copper removal from printed circuit board etching solutions employing either cupric chloride or ammoniacal etchant. In a cell divided by a cation exchange membrane the etching process is essentially reversed. In case of the cupric chloride etchant the etchant solution is pumped to the anode, the processes are at the



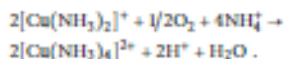
Copper ions generated at the anode pass through the membrane and are deposited at the cathode in dendritic form, they are recovered from the bottom of the cell. The respective etching process is



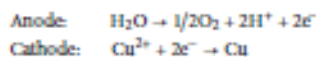
In the etching process employing a slightly acidic ammoniacal etchant the etching reaction is



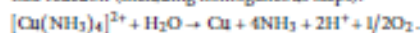
and



The etchant solution is pumped to the cathode of the regeneration cell, electrode reactions are at the



Cell reaction (including homogeneous steps):



In the CEER cell the etchant is pumped to the cathode where copper removal proceeds.

Ref.: [i] Fletcher D, Walsh FC (1993) *Industrial electrochemistry*. Blackie Academic & Professional, London

RH

Cell constant — The specific conductivity of matter is defined as the conductivity measured between two conducting plates (electrodes in measurements of ionic conduction) of 1 cm² area spaced at a distance of 1 cm (→ conductivity cell). In practical construction these geometrical specifications are not easily obtained, and the actual dimension may differ. To convert conductivity data obtained with a real cell having different geometric dimension the conductivity χ_{cell} of a solution with well-known specific conductivity χ_{ref} is measured with this cell. Taking the reference value χ_{ref} the cell constant κ is obtained by $\kappa = \chi_{\text{ref}}/\chi_{\text{cell}}$. Subsequently measured conductivity χ_{cell} employing this cell can easily be converted into specific conductivities χ according to $\chi = \kappa\chi_{\text{cell}}$.

Ref.: [i] Bard AJ, Faulkner L (2000) *Modern electrochemistry*. Springer, New York

RH

Cell diagram — A galvanic cell is represented by a diagram. Thus, the chemical cell, consisting of an aqueous

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