Electrochemical Basics

1 Electrolytes and Electrodes Electrolyte Conductivity

Potential, Voltage

2 Electrochemical Reactions, Metal Deposition Current, Current Density, Charge quantities Faraday's Law, Current Efficiency, Deposition Rate

3 Overvoltage and Parameters Charge Transfer, Mass Transport

4 **Properties of the Plated Layers**

5 Overview of our Electroplating Processes Zinc, Copper, Nickel, Chromium, Tin

The electrolyte solution consists of **solvents** and therein dissolved **mobile charge carriers**.







Solvent Molecules ar	oments				
	M	ρ	μ		\mathcal{F}
	g/mol	g/cm ³	10 ⁻³⁰ Cm	10 ⁻⁶ Cm/l	
water	18,015	1,000	6,2	207	
ammonia	17,031	0,682	4,9	118	
methanol	32,042	0,791	5,7	84	
aceton	58,080	0,790	9,6	79	
acetic acid	60,053	1,049	5,8	61 🤇	
dichloromethane	84,932	1,327	5,3	50	
lactic methyl ester	104,106	1,086	7,2	45	Le la
diethylether	74,123	0,714	3,8	22	\frown
cyclohexane	84,161	0,778	0,0	0	

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Solvated cations and anions are the **dissolved mobile** charge carrier.





- Small solvent molecules with a high dipole moment solvate the ions strongly and can therefore dissolve them out of the crystal formation of the respective salt.
- Solvent molecules with a small dipole moment can dissolve weak salts only.
- Big solvent molecules are forming voluminous solvate sphere, and the ions are less mobile.
- Cations with small ion radius are producing a strong electrical field and consequently have a particularly voluminous solvate sphere. Thus, the mobility increases in the order Li+, Na+, K+, Rb+.
- In aqueous electrolytes, the charge of protons and hydroxide ions can move by a jump mechanism along the hydrogen brigde bonds of the water molecule chains. Therefore, the mobility is significantly higher.



The **Electrolyte Conductivity** depends on the number of the dissolved charge carriers as well as on their charge and mobility.

- With a rise of concentration, the number of charge carriers and consequently the conductivity increases.
- With increasing concentration, the mobility of the ions diminishes (hindering), also more neutral ion pairs are formed, which are not contributing to the conductivity (uncomplete dissociation).
- By these opposite effects, the electrolyte conductivity in general finally decreases at very high concentrations.
- At higher temperature, the mobility is greater (viscosity) and the conductivity is higher.
- Because of the special wandering mechanism of the proton and hydroxyde ion charges, acids and lyes have a particularly good conductivity (extra conductivity of protons and hydroxide ions).
- Also salt melts are ion conductors. Compared with electrolytic solutions, their electrical conductivity is extremely higher (highest concentration, smallest charge carriers).
- There are also solid ion conductors (solid electrolytes, e.g. β -Al₂O₃, sodium ion conductor)



The **electrochemical electrode** consists always of a electron conducting phase (metal, semiconductor, graphite,...), on which is **bordering** an ion conducting **phase** (electrolyte solution, salt melt, solid electrolyte.

For the electrochemical processes, the **phase boundary** between electrode and electrolyte plays a decisive role.

- In general, the energetic state of a given particle is different in the electrode and in the electrolyte.
- There will always be particles, also charged particles, which are passing the phase boundary in one or the other direction.
- If a particle meets a lower energy level, it transfers its surplus energy, and cannot come back to its original level.
- Wandering charged particles leave their countercharge (with metal electrodes: electrons in the electrode resp. anions in the electrolyte).
- By this way, from surplus charges on both sides of the phase boundary, an electrical double layer is formed, which is causing an electrical potential difference.

Electrolytes and Electrodes: Potentials



- Electrical potentials for electrically charged particles are contributing to their total energy according: $E = E_0 + zF \cdot \phi$.
- In the equilibrium, the potential difference between the phases are just big enough to balance the energy difference.
- In a dynamic equilibrium, the same number of particles is wandering in both directions, on one hand driven by the concentration gradient (diffusion), on the other hand by the energy slope (field). Both contributions to the particle current j are compensating themselves:

$$j_{Diff} = j_{Feld}$$

$$-D\frac{dc}{dx} = -c \cdot u \cdot \frac{dE}{dx} = -c \cdot \frac{D}{RT} \cdot zF \frac{d\Delta\varphi}{dx}$$

$$dc = c \cdot \frac{zF}{RT} \cdot d\Delta\varphi$$

$$\Delta\varphi = \frac{RT}{zF} \int d\ln c$$

$$\Delta\varphi_0 = \Delta\varphi_{00} + \frac{RT}{zF} \ln c$$

This is the Nernst Equation, describing the dependancy of the potential difference $\Delta \phi_0 = \phi_2 - \phi_1$ (Galvani voltage) of the concentration of the participating particles in the respective phase of the equilibrium.

Electrolytes and Electrodes: Voltage

It is technically impossible to measure the Galvani voltage $\Delta \phi$. If one combines an electrode/electrolyte system with a second one to an electrochemical cell, a voltage U between the both electrochemical electrodes can be measured, indeed. In the simplest case, two different electrodes (Zn und Cu) dip into an electrolyte:

Cu 504²⁻ 7n2+ Cu²⁺

Cu | Cu²⁺ Zn²⁺ Zn Me Me Φ1 $\varphi_2 | \varphi_3$ Φ4 φ5 **φ**6 $[J = \Delta \phi_{3-2} + \Delta \phi_{4-3} + \Delta \phi_{5-4} = \phi_{5} - \phi_{2}$

- The Galvani voltages at the single phase boundaries add to the cell voltage.
- The potential-determining reactions are Cu | Cu²⁺: Cu²⁺ + 2 e⁻ \leftrightarrow Cu $Zn | Zn^{2+}$: $Zn^{2+} + 2e^{-} \leftrightarrow Zn$
- The Galvani potentials and the cell voltage are a measure for the free reaction enthalpies of the respective reactions. However, only the cell voltage is measurable.
- If a predicate about the **potential** at an electrode is desired, the electrode is linked with a standard reference electrode and the voltage is measured.
- The potential of the standard hydrogen electrode was assumed arbitrarily as **0**. The potential-determining reaction is: H₂|H+ H+ + e⁻ \leftrightarrow 1/2 H₂
- The **electromotive serie** was set up by voltage measurements against the standard hydrogen electrode as the reference electrode.

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Standard potentials at 25 °C in solutions of the activity 1 at 1013.15 mbar

Li/Li+	-3.05	H_2/H^+	0
Na/Na+	-2.71	Cu/Cu ²⁺	+0.34
Mg/Mg+	-2.38	0 ₂ /OH	+0.40
A /A ³⁺	-1.71	Hg/Hg+	+0.80
H ₂ ,OH ⁻	-0.83	Ag/Ag+	+0.80
Zn/Zn ²⁺	-0.76	O ₂ ,H+	+1.23
Cr/Cr ³⁺	-0.71	Cl ₂ /Cl ⁻	+1.37
Fe/Fe ²⁺	-0.41	Au/Au+	+1.42
Ni/Ni ²⁺	-0.23	F_2/F^-	+2.85
Sn/Sn ²⁺	-0.14		
Pb/Pb ²⁺	-0.13		
Fe/Fe ³⁺	-0.05		



Electrical Charge has the unit Coulomb resp. Ampère second (1 C = 1 As).

$$Q = \int I dt$$

Electrical Current is the transfer of electrical charges per time unit.

$$I = \frac{dQ}{dt}$$

Electrical Current Density is the transport of charges per time and area.

$$j = \frac{I}{A} = \frac{dQ}{A \cdot dt}$$

1 mol elementary charges are $6.02205 \cdot 10^{23}$ pieces each at $1.602192 \cdot 10^{-19}$ As = 96485 As. This was **Faraday's Law** with the constant **F** = **96485 As/mol**. Electrode processes are always connected with a charge transfer through the phase boundary between electrode and electrolyte.

The direction of the charge transfer determines whether an electrode works reducing or oxidising.



- At the cathode negative charges (electrones or anions) are transfered into the electrolyte and/or positive cations are moved out of the electrolyte into the electrode. Cathodic processes are reduction reactions. In driven processes (e.g. electroplating) the cathode is negative.
- At the **anode** positive cations are transfered into the electrolyte and/or negative charges (electrones or anions) are moved out of the electrolyte into the electrode. Anodic processes are **oxidation** reactions. In driven processes (e.g. electroplating) the anode is **positve**.

Attention: In a current supplying "galvanic" cell (e.g. batterie, fuell cell , zinc generator) the cathode is positive and the anode is negative.

An electrode process comes never alone. For the charge balance always a second process with reverse signs is necessary, which must run at the same time and with the same reaction rate. To a cathodic reaction belong always (at least) one anodic and vice versa.

The overlay of the electrode processes results in the **Cell Reaction**:

e 2 Cu SO₄²⁻ Cu²⁺ Zn²⁺

O Current supplying cell (batterie)

Anodic oxidation:	Zn			\rightarrow	Zn2+	+	2 e-
Cathodic reduction:	Cu ²⁺	+	2 e-	\rightarrow	Cu		
Cell reaction:	Zn	+	Cu ²⁺	\rightarrow	Zn ²⁺	+	Cu
Ø Driven (electrolytic) cell							
Anodic oxidation: <u>Cathodic reduction:</u>	Cu Zn ²⁺	÷	2 e-	\rightarrow \rightarrow	Cu ²⁺ Zn	+	2 e-
Cell reaction:	Cu	+	7n2+	\rightarrow	Cu2+	+	7n

For Example zinc is a non precious metal, its standard potential is located negatively from the hydrogen. Therefore the cathodic zinc deposition takes place at a potential, at which also hydrogen can be evolved by cathodic reduction of water. This means that at one electrode two processes occur at the same time and the current divides itself on this two reactions. Therefore the **current efficiency** for zinc is smaller than 100 % in this case.

The **deposition rate** of metals results according to Faraday's law from the factor of **current efficiency** and **current density**. Example: cathodic zinc deposition with 0.75 A/dm² = $0.75 \text{ A}/100 \text{ cm}^2$ with a current efficiency of 95 %

1. Deposited amount of matter (number of moles) per surface and time (surface-specific reaction rate):

$$\frac{dn}{Adt} = \frac{\gamma}{zF} \cdot \frac{dQ}{Adt} = \frac{\gamma}{zF} \cdot j = \frac{0.95 \text{ mol} \cdot 0.75 \text{ A}}{2 \cdot 96485 \text{ As} \cdot 100 \text{ cm}^2} = 36.923 \cdot 10^{-9} \frac{\text{mol}}{\text{cm}^2 \text{ s}}$$

2. Deposited mass per surface and time (mol mass of zinc is involved):

$$\frac{dm}{Adt} = M \cdot \frac{dn}{Adt} = \frac{65.39 \text{ g} \cdot 36.923 \cdot 10^{-9} \text{ mol}}{\text{mol} \text{ cm}^2 \text{ s}} = 2.4144 \frac{\mu \text{g}}{\text{cm}^2 \text{ s}}$$

3. Deposited layer thickness per time (density of zinc is involved):

$$\frac{dx}{dt} = r = \frac{\frac{dm}{Adt}}{\rho} = \frac{2.4144 \ \mu g \ cm^3 \ 60 \ s \ 10^4 \ \mu m}{cm^2 s \ 7.14 \ g \ min \ cm} = \frac{0.20 \ \mu m \ / \ min}{2.40 \ \mu m \ m}$$

Overvoltages and Influences: Charge Transfer



$$E_{A,ox} = E_{A,0} - \alpha \cdot zF \cdot \Delta \varphi$$
$$E_{A,red} = E_{A,0} + (1-\alpha) \cdot zF \cdot \Delta \varphi$$

The higher the voltage, the higher current and deposition rate, **or...**

- The current must in any case pass the **phase boundary** between electrode and electrolyte
- In the case of the cathodic reduction of metal cations at a metal cathode electrons will transfer from the metal to the cations into the electrolyte.
- The **charge transfer** over the phase boundary must overcome an activation energy threshold; Arrhenius activated complex theory:

$$j_{ox} = zF \cdot k_{ox} \cdot c_{red} \cdot \exp\left(-\frac{E_{A,0}}{RT} + \alpha \frac{zF}{RT}\Delta\varphi\right)$$

$$\left(-\frac{E_{A,0}}{RT} + \alpha \frac{zF}{RT}\Delta\varphi\right)$$

$$j_{red} = zF \cdot k_{red} \cdot c_{ox} \cdot \exp\left(-\frac{E_{A,0}}{RT} - (1-\alpha)\frac{zF}{RT}\Delta\varphi\right)$$

• in the equilibrium applies:

$$j_{0,ox} = |j_{0,red}| = j_0$$
 $k_{0,ox} = k_{0,red} = \exp\left(-\frac{E_{A,0}}{RT}\right)$

• and otherwise (with
$$\eta$$
 = overvoltage):
 $j = j_{ox} + j_{red}$ and $\Delta \varphi = \eta + \Delta \varphi_0$

Overvoltages and Influences: Charge Transfer



During the cathodic deposition of e.g. zinc the electrolytic solution in direct proximity of the cathode becomes impoverished. The zinc ions are transported by diffusion from the solution inside to the phase boundary, and the deposition rate cannot run faster than the **mass transport**. Finally it comes to the formation of a **diffusion limiting current**.



Overvoltages and Influences: Current Voltage Curves



Current voltage curves, 20 mV/s, rotating Au disk electrode, 0.196 cm², 1600 rpm, non cyanide alkaline zinc electrolyte (10 g/l Zn, 120 g/l NaOH)

Im allgemeinen wird ein dekoratives Aussehen der Überzüge gefordert. Dazu gehört in erster Linie der **Glanz**. Die Schicht soll natürlich homogen sein.

Zwecks Korrosionsschutz und Abriebfestigkeit ist eine gewisse **Schichtdicke** erforderlich. Je nach Verfahren werden $0,3 - 30 \ \mu m$ (bei Hartchrom bis 1000 $\ \mu m$) abgeschieden.

Die Schichten müssen **spannungsarm** und **haftfest** auch unter nachträglicher Verformung sein. Duktile Schichten sind in dieser Beziehung unproblematischer. Bei Hartchrom ist vor allem die **Härte** ausschlaggebend.

Die Schichtdickenverteilung, die sogenannte **Metallverteilung** sollte möglichst homogen sein.



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SurTec	821	758	704	728	866	869	857	871
Elektrolyt- typ	sauer	schwach sauer	alkalisch cyanidfrei	alkalisch cyanidisch	cyanidisch	sauer	Watt's	misch- sauer
	Sulfat	Chlorid	Hydroxid	Cyanid	Cyanid	Sulfat	Sulfat/ Chlorid	Chrom- säure
рН	<< 1	5	> 14	> 14	> 14	< 1	4	<< 1
Vorteil	Glanz	schnelle Abschei- dung	beste Metall- verteilung	wenig kritisch	auf allen Materi- alien	Glanz, Eineb- nung	Spitzen- glanz, Einebnung	Farbe, Glanz
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Ausbeute	95 %	98 %	70-80 %	65 %	65 %	100 %	95 %	12 %
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