Reakcije u hemijskim izvorima struje

Predavanje 10, 07.04.2021.

Udžbenik: S. Mentus, Elektrohemija, 2008, strane 120-126

(NAPOMENA: Za ispit dolaze u obzir samo izvori koji su obrađeni u udžbeniku)

Hemijski izvori struje – opšte osobine

Galvanski element koji koji služe kao prenosivi izvori električne energije

- niska cena,
- najmanje moguće zagađivanje životne sredine,
- mala gustina,
- veliki napon otvorenog kola,
- brze elektrodne reakcije,
- veliki stepen iskorišćenja aktivnih materijala,
- mali stepen samopražnjenja (međusobnog reagovanja aktivnih materijala).

Hemijski izvori struje – opšte osobine

Napon baterije

Kapacitet
3 sata daje 1000 mA (1A)
3000 sati daje 1 mA
(i bilo šta između, u teoriji)

Hemijski izvori struje – opšte osobine

tesla car weight of batteries

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About 1,550,000 results (0.84 seconds)

1,200 lb

The 85 kWh battery pack weighs 1,200 lb (**540 kg**) and contains 7,104 lithium-ion battery cells in 16 modules wired in series (14 in the flat section and two stacked on the front).

en.wikipedia.org › wiki › Tesla_Model_S

Tesla Model S - Wikipedia

Gustine snage 85000 Wh / 540 kg

= 157 Wh/kg

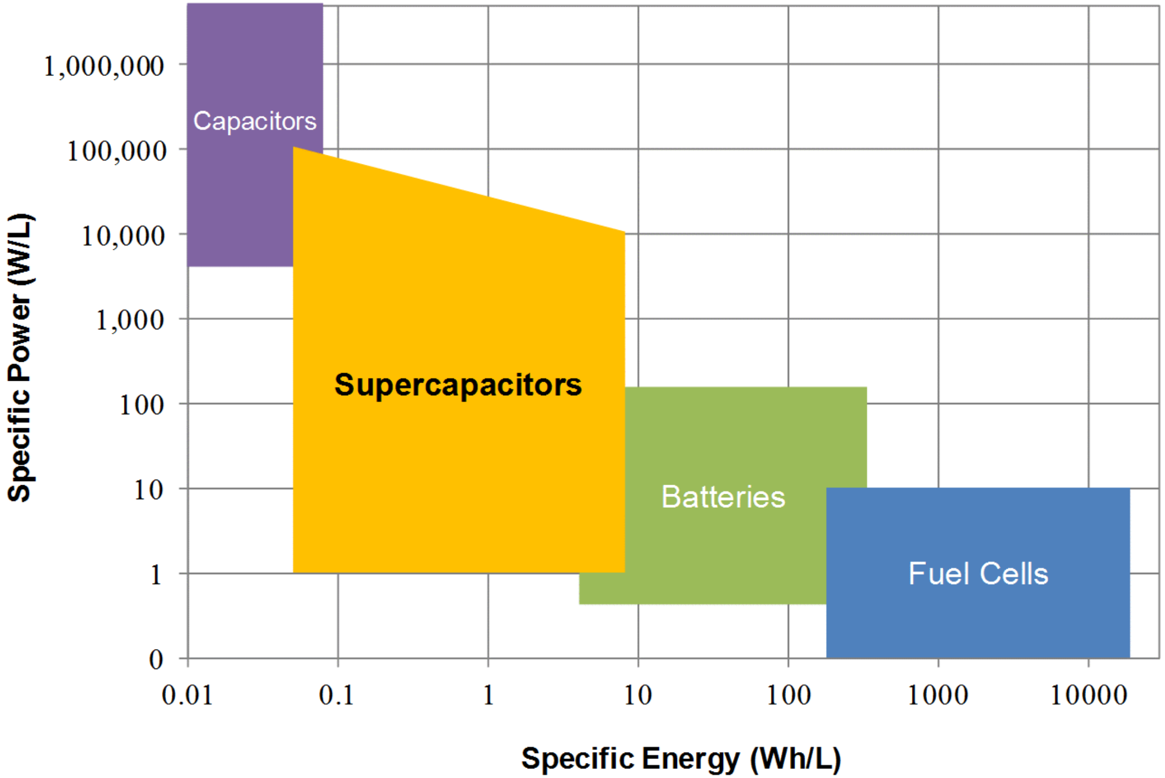
Jedna Li-ion ćelija 12 Wh

(ako radi na 4 V onda ima 3000 mAh)

Konverzija **Wh** u **mAh**
Formula je (**Wh**)*1000/(V) =(**mAh**).
1.5**Wh** baterija sa nominalnih 5V, snaga je 1.5**Wh** * 1000 / 5V = 300mAh.

Hemijski izvori struje – podela

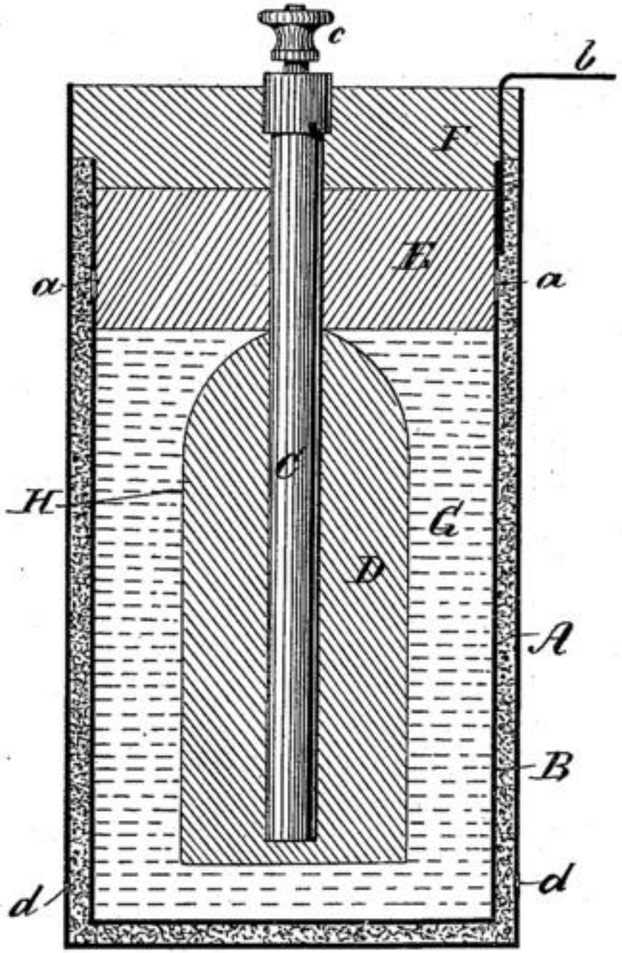
- Primarni (primarne baterije)
- Sekundarni (akumulatori)
- Gorivne ćelije (elektrokataliza)
- + Elektrohemijski kondenzatori (kasnije)



Primarni izvori

- Suvi element / Leklanšeova ćelija / Zn-C baterija / Zn-MnO2 baterija

- Najstariji hemijski izvor struje



Primarni izvori

Suvi element / Leklanšeova ćelija / Zn-C baterija / Zn-MnO2 baterija (1.5 V)

Na anodi:

$2Zn + 4NH_4Cl \rightarrow ZnCl_2 + Zn(NH_3)_4Cl_2 + 4H^+ + 4e^-$

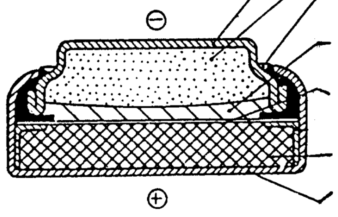
Na katodi:

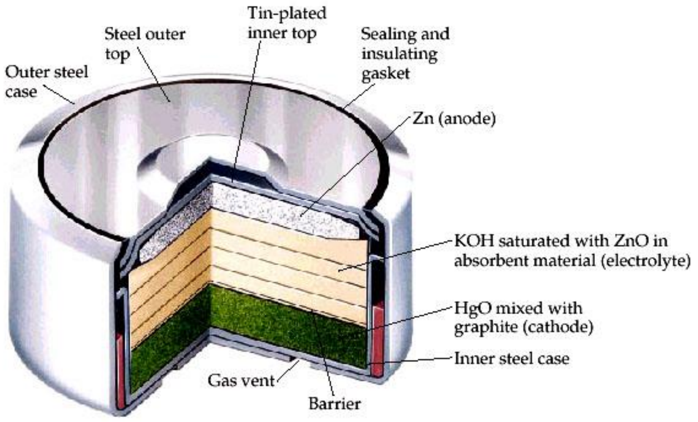
$4MnO_2 + 4H^+ + 4e^- \rightarrow 4MnO \cdot OH$

$2Zn + 4NH_4Cl + 4MnO_2 \rightarrow ZnCl_2 + Zn(NH_3)_4Cl_2 + 4MnO \cdot OH$

Primarni izvori

Zn-HgO baterija (minijaturna baterija, coin cell, button cell)



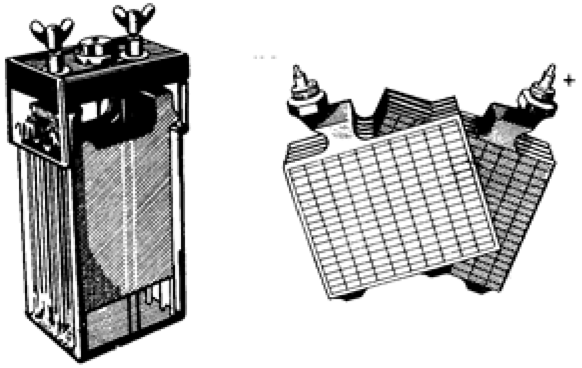


$$Zn + HgO = ZnO + Hg$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{2F} \ln \frac{a_{ZnO} a_{Hg}}{a_{HgO} \cdot a_{Zn}}$$

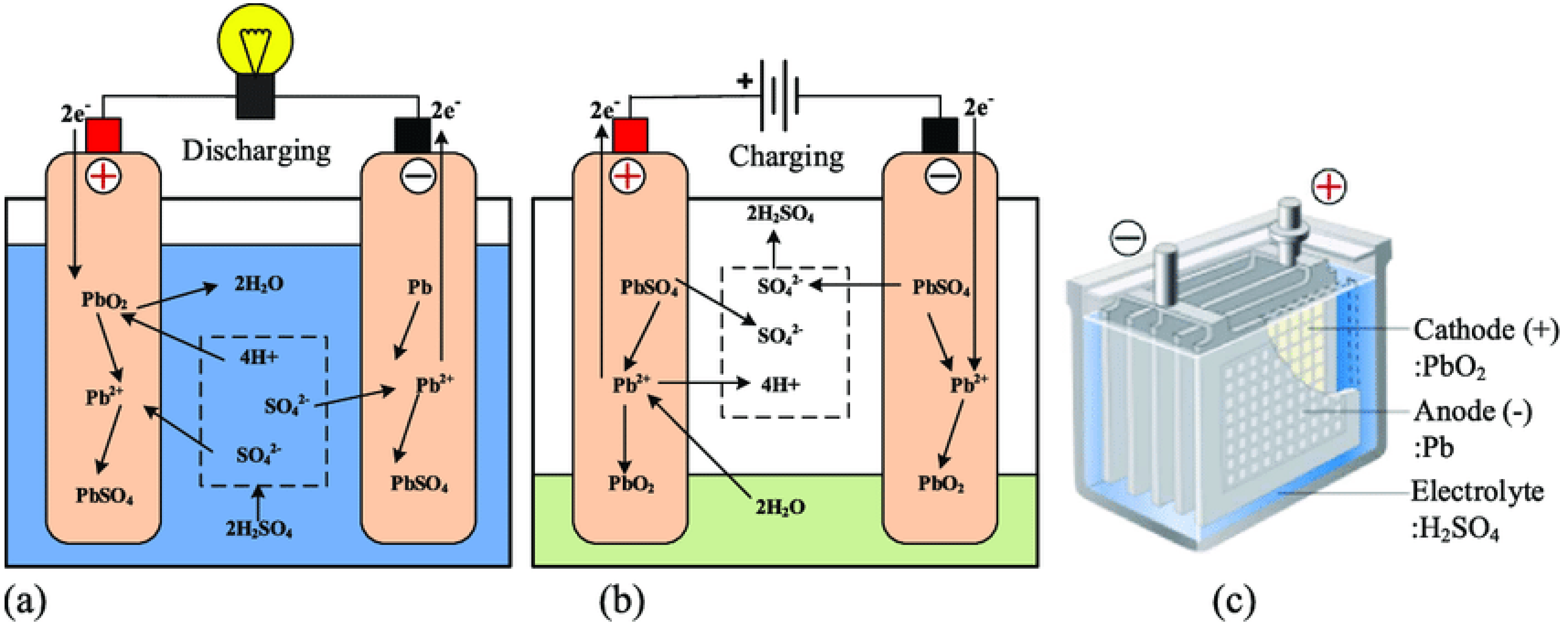
$\varepsilon^0 = 1{,}36$ V

Sekundarni izvori



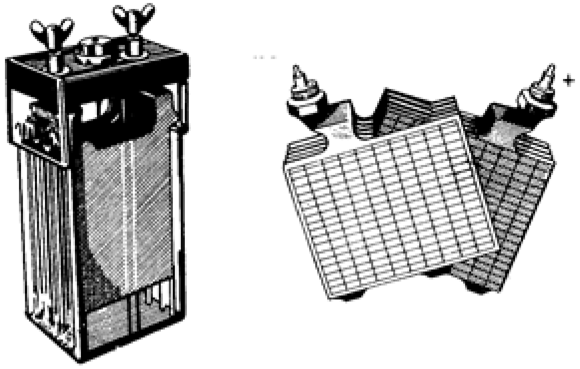
- Olovni akumulator (~2 V)

$Pb \mid H_2SO_{4,}\ H_2O \mid PbO_2,Pb$



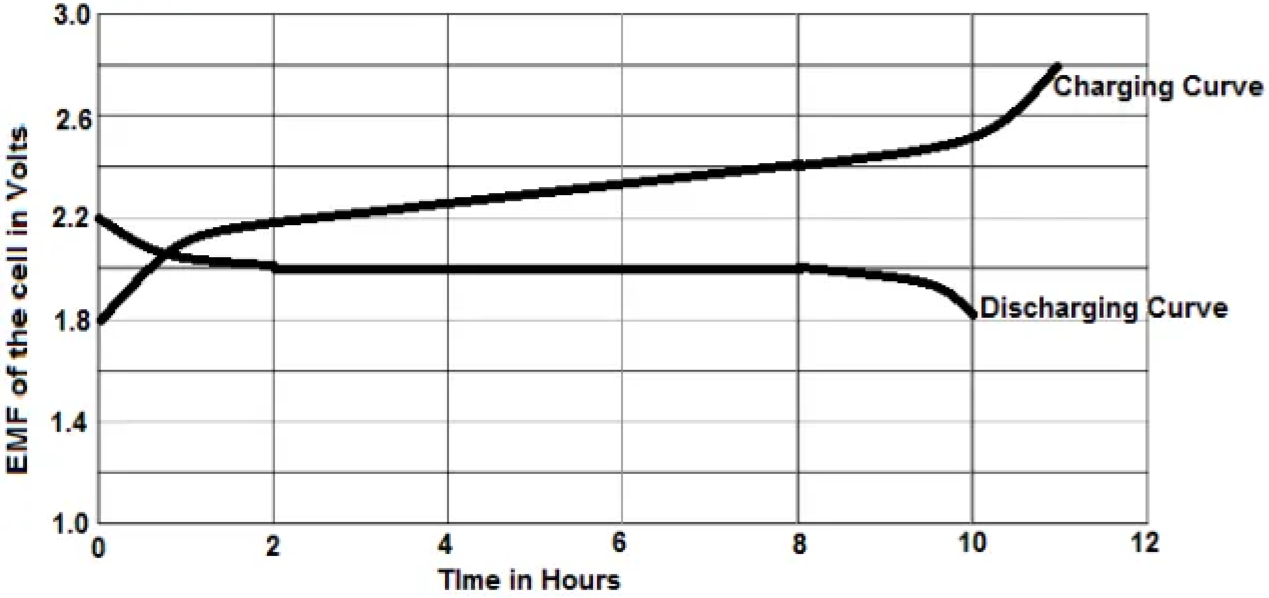
Sekundarni izvori

- Olovni akumulator (~2 V)



$Pb \mid H_2SO_4, H_2O \mid PbO_2, Pb$

$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$



$$\varepsilon = \varepsilon^0 - \frac{RT}{2F} \ln \frac{a_{PbSO_4}^2 \cdot a_{H_2O}^2}{a_{Pb} \cdot a_{PbO_2} \cdot a_{H_2SO_4}^2}$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F} \ln \frac{a_{H_2O}}{a_{H_2SO_4}}$$

Približno konstantno

Sekundarni izvori

- Alkalni akumulatori (1.35 V)

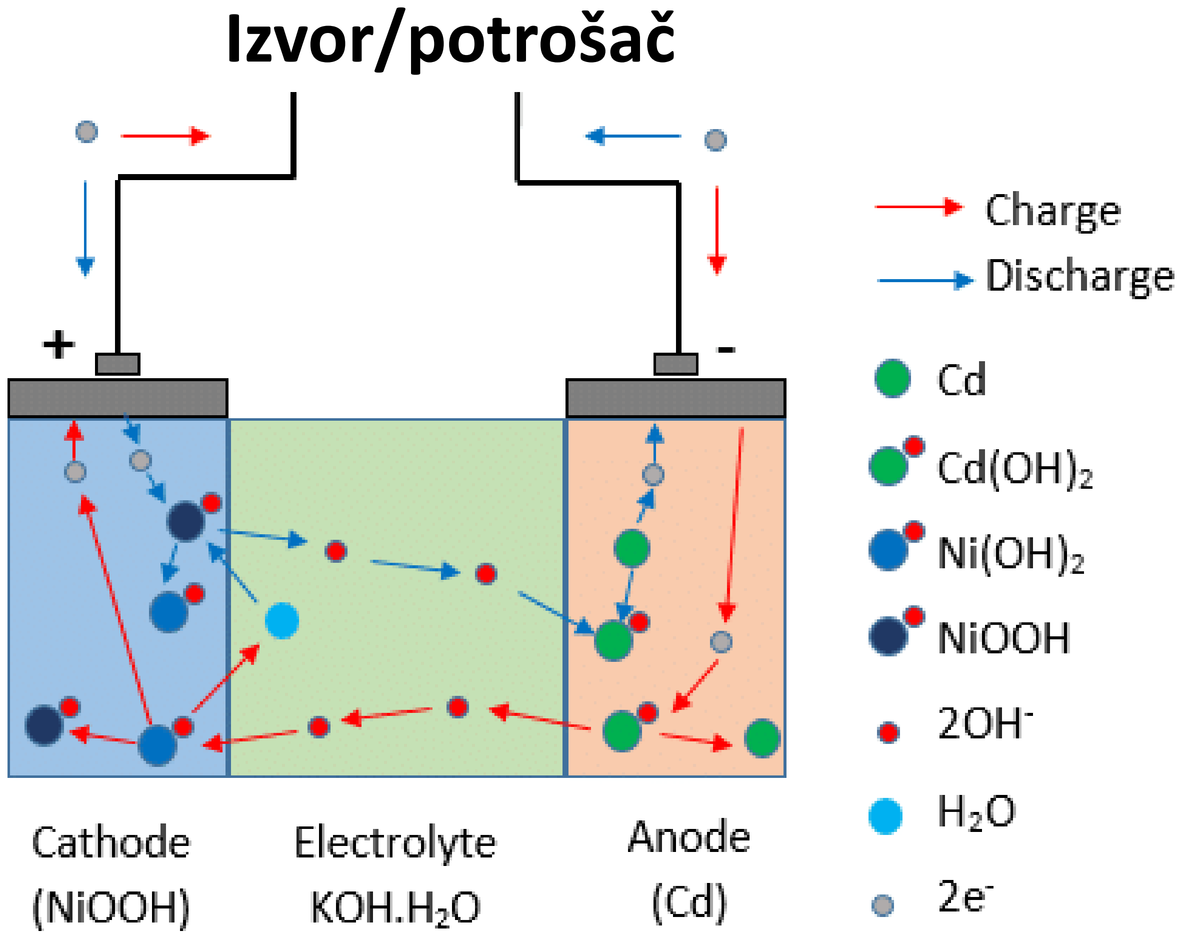
Fe | KOH, H_2O | $Ni(OH)_2$, $Ni(OH)_3$,Ni

Cd | KOH, H_2O | $Ni(OH)_2$, $Ni(OH)_3$,Ni

$Fe + 2Ni(OH)_3 = Fe(OH)_2 + 2Ni(OH)_2$

$Cd + 2Ni(OH)_3 = Cd(OH)_2 + 2Ni(OH)_2$

$$\varepsilon = \varepsilon^0 - \frac{RT}{zF} \ln \frac{a^2_{Ni(OH)_2} \cdot a_{M(OH)_2}}{a^2_{Ni(OH)_3} \cdot a_M}$$



Sekundarni izvori

- Alkalni akumulatori (1.35 V)

$$\varepsilon = \varepsilon^0 - \frac{RT}{zF} \ln \frac{a^2_{Ni(OH)_2} \cdot a_{M(OH)_2}}{a^2_{Ni(OH)_3} \cdot a_M}$$

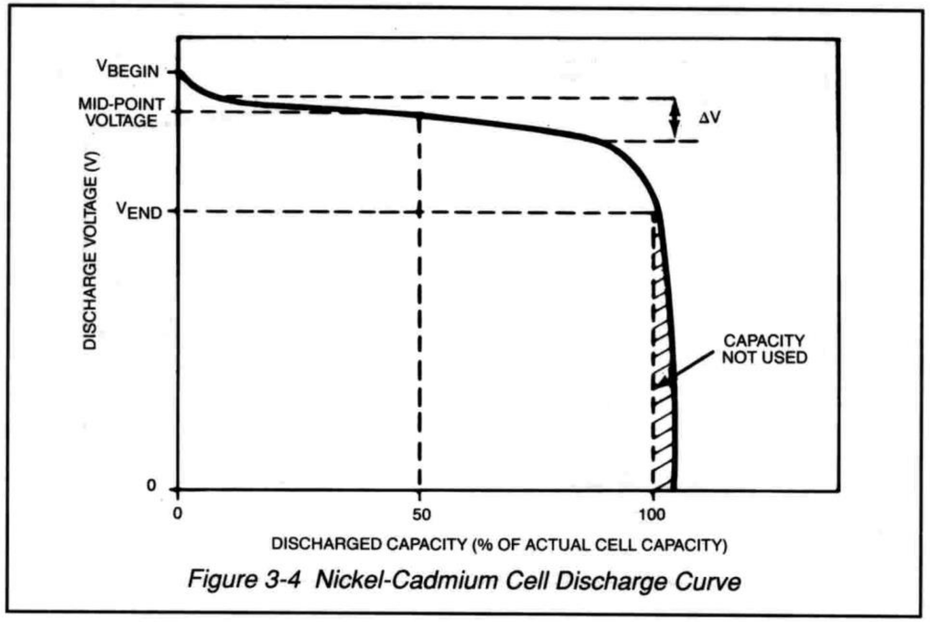
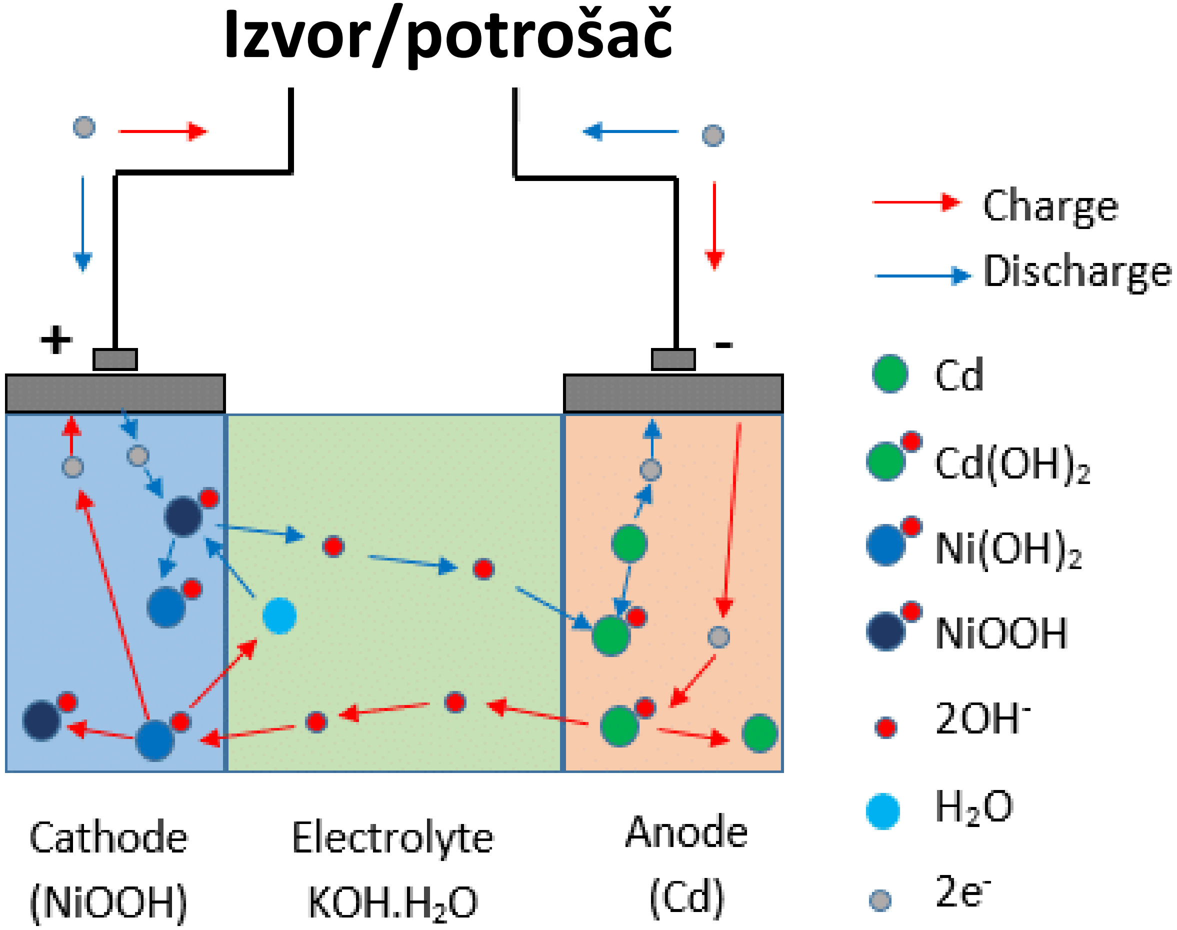


Figure 3-4 Nickel-Cadmium Cell Discharge Curve

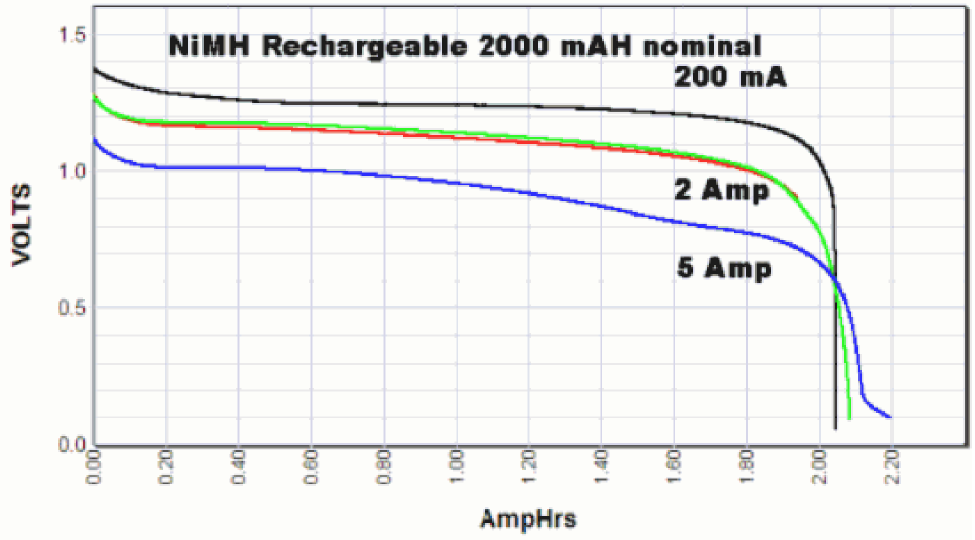


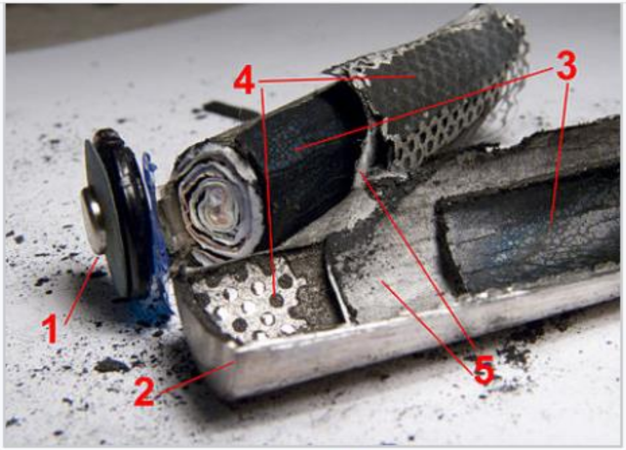
Još neki tipovi sekundarnih izvora

- Ni-MH baterije

(-) $H_2O + M + e^- \rightleftharpoons OH^- + MH$

(+) $Ni(OH)_2 + OH^- \rightleftharpoons NiO(OH) + H_2O + e^-$



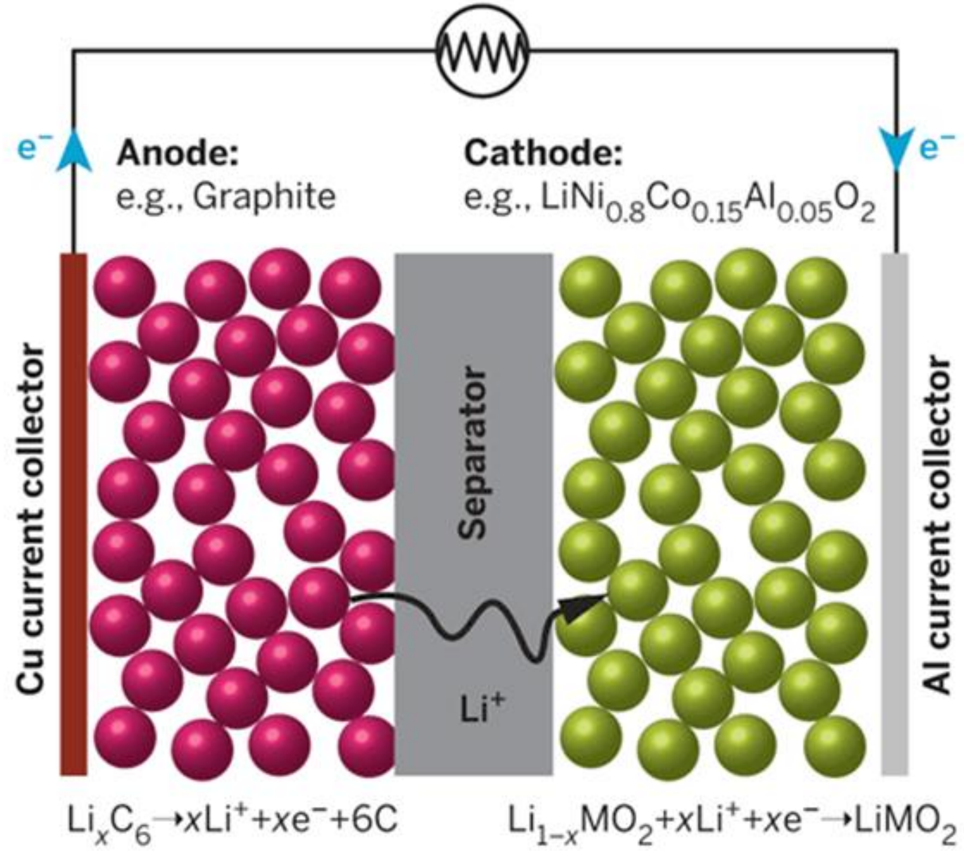


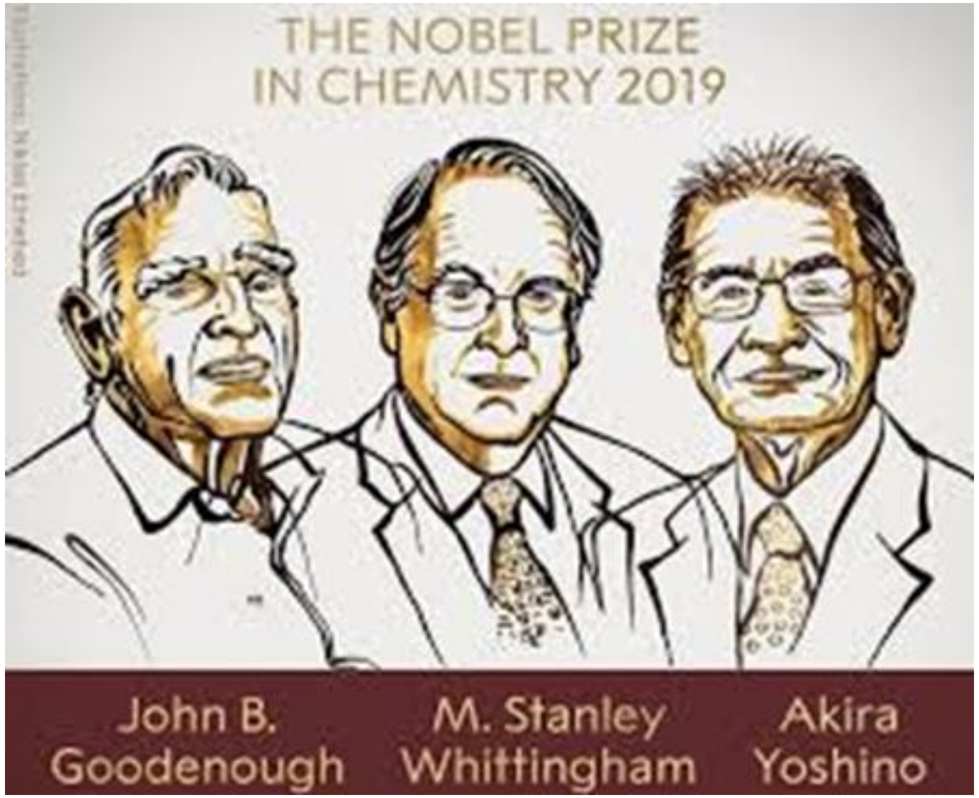
Disassembled NiMH AA battery:

1. Positive terminal
2. Outer metal casing (also negative terminal)
3. Positive electrode
4. Negative electrode with current collector (metal grid, connected to metal casing)
5. Separator (between electrodes)

Još neki tipovi sekundarnih izvora

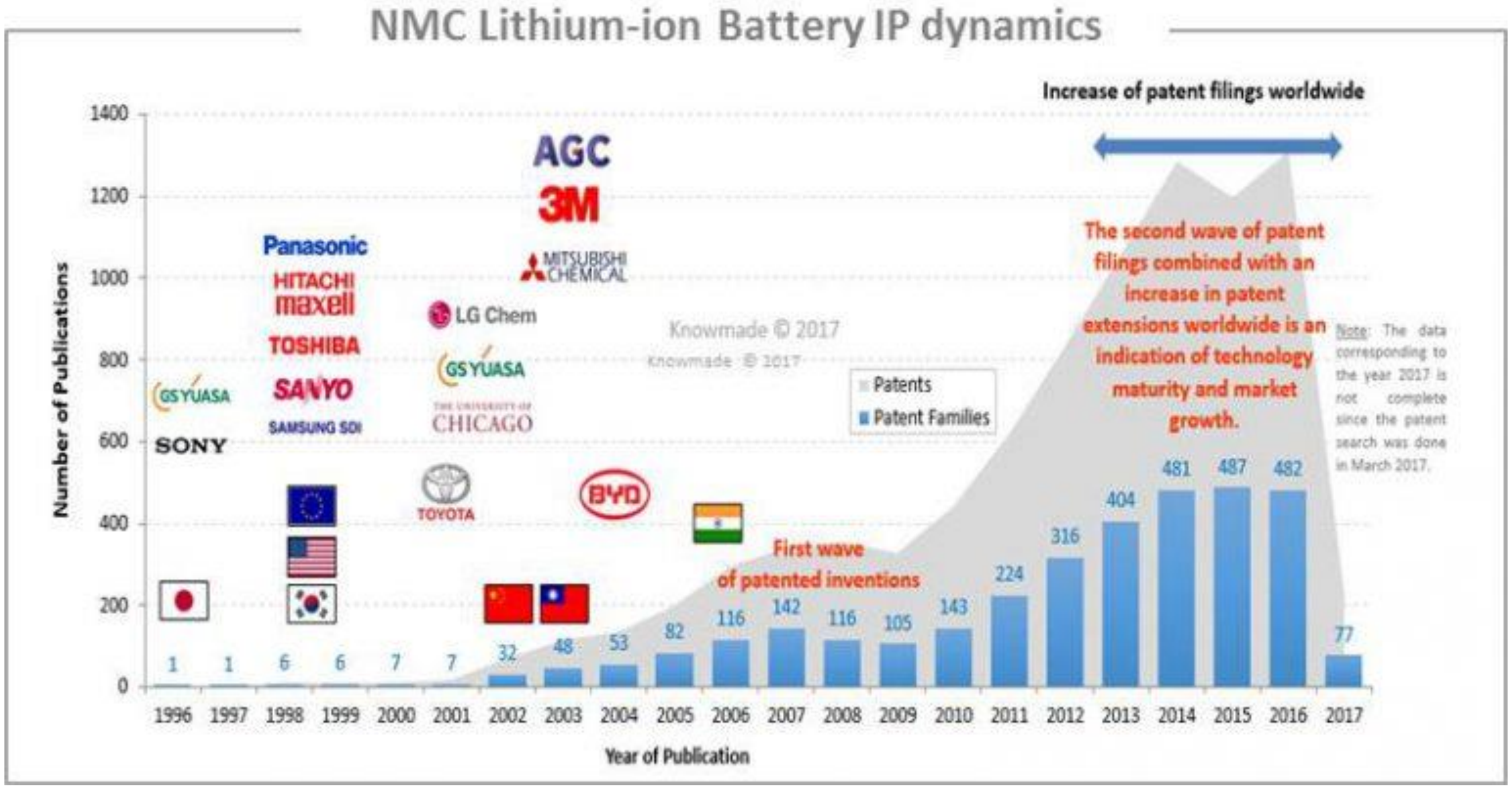
- Li-ionske baterije





Još neki tipovi sekundarnih izvora

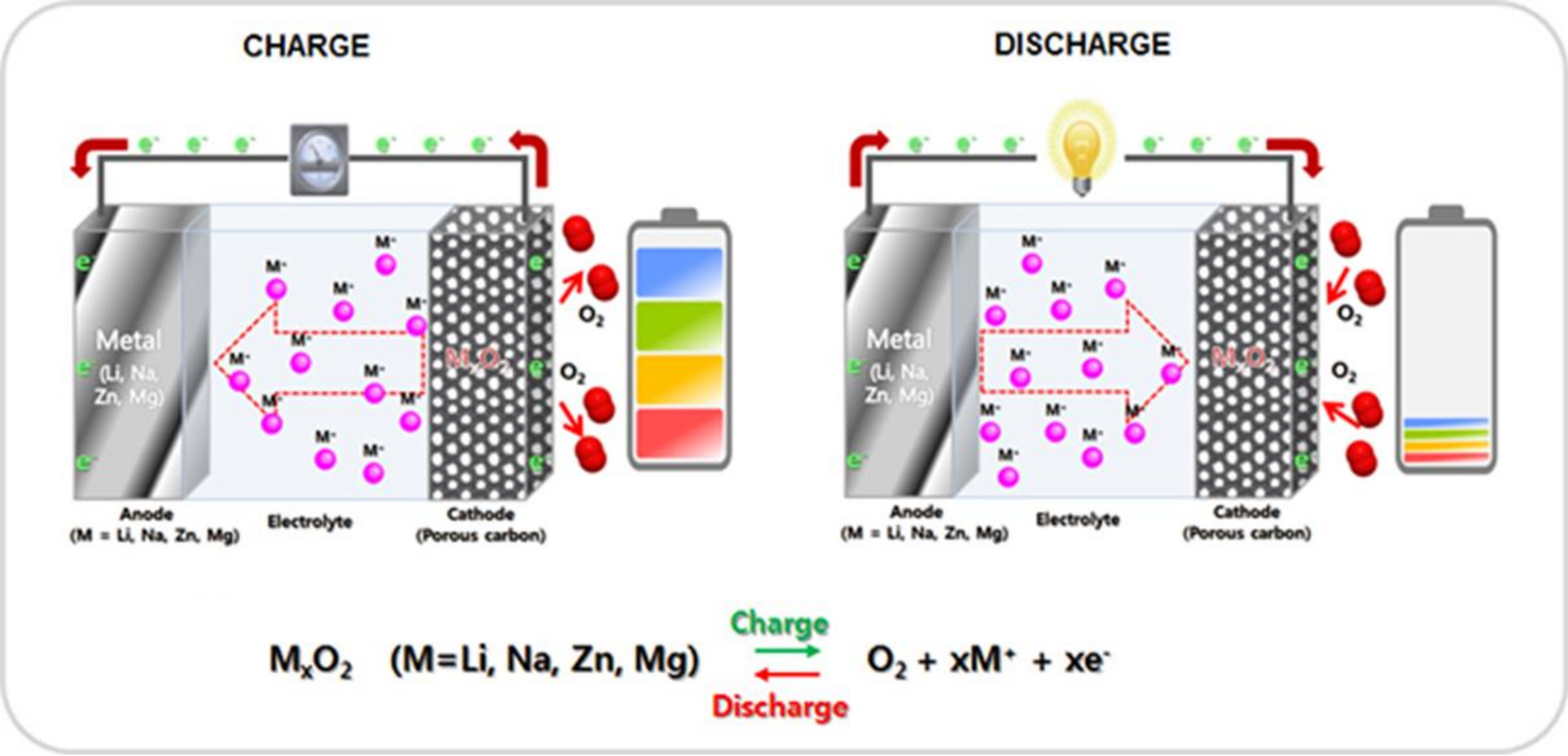
- Li-jonske baterije



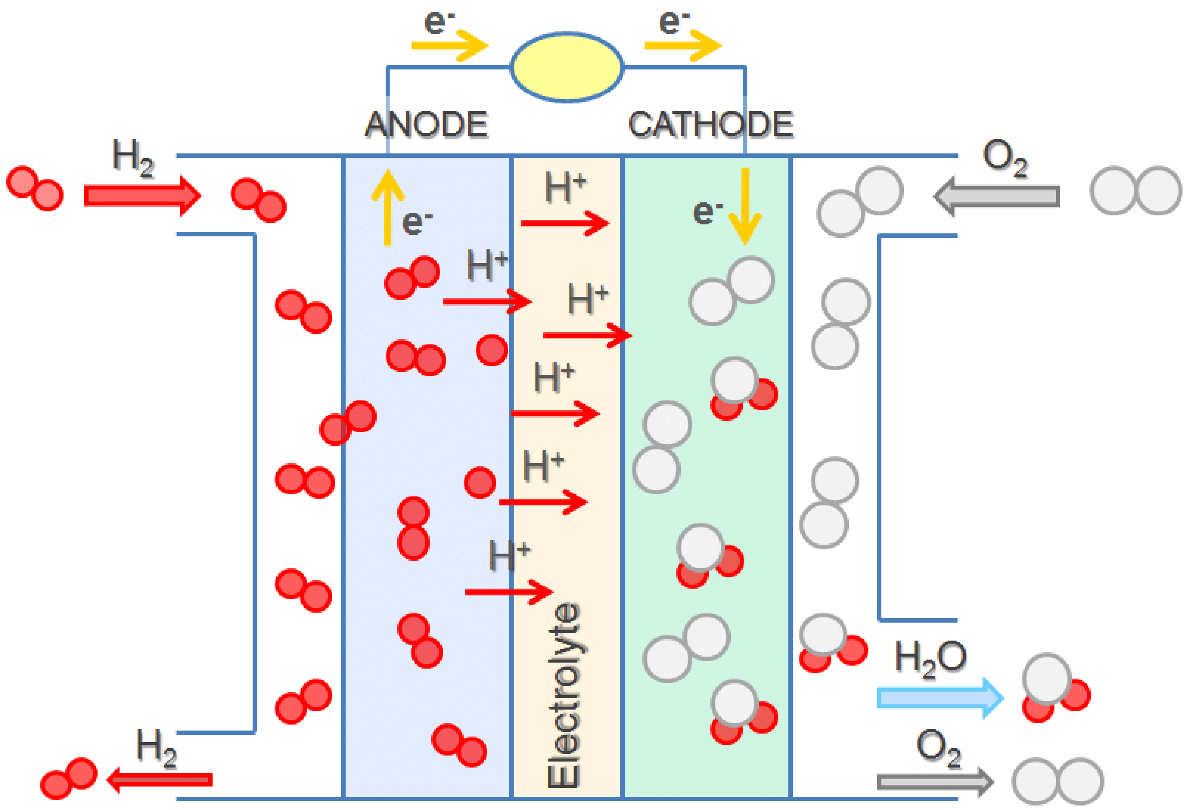
https://www.knowmade.com/downloads/nmc-lithium-ion-batteries/

Još neki tipovi sekundarnih izvora

Metal-vazduh baterije



Gorivne ćelije



PEMFC

Anoda – oksidacija H_2
Katoda – redukcija O_2

Standadi veličina

Korisni linkovi

- https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_(Zumdahl_and_Decoste)/11%3A_Electrochemistry/11.5%3A_Batteries

- https://en.wikipedia.org/wiki/List_of_battery_sizes

- **DODATNO ZA ZAINTERESOVANE**
- http://www.ffh.bg.ac.rs/wp-content/uploads/2019/04/Doktorske-studije-Ivana-Stojkovic-Simatovic.pdf (opšte o Li-jonskim baterijama, predavanje Prof. Ivane Stojković-Simatović na doktorskim studijama)

- http://www.ffh.bg.ac.rs/wp-content/uploads/2019/04/PhD-PtC.pdf (platinski katalizatori za gorivne ćelije, predavanje Prof. Nemanje Gavrilova na doktorskim studijama)

Merenje standardne elektromotorne sile, primene

Predavanje 11.

Udžbenik: S. Mentus, Elektrohemija, 2008, strane 125-132

Šta do sada znamo?

$\Delta G = -nF\varepsilon$

$$\varepsilon = \varepsilon^0 - \frac{RT}{nF}\ln\prod a_i^{\nu_i}$$

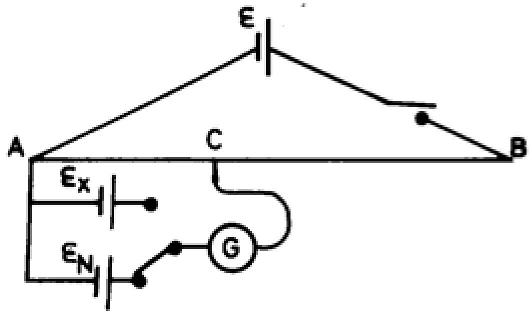
$$\varepsilon^0 = \frac{-\Delta G^0}{nF}$$

Standardna elektromotorna sila → **Termodinamika reakcije**

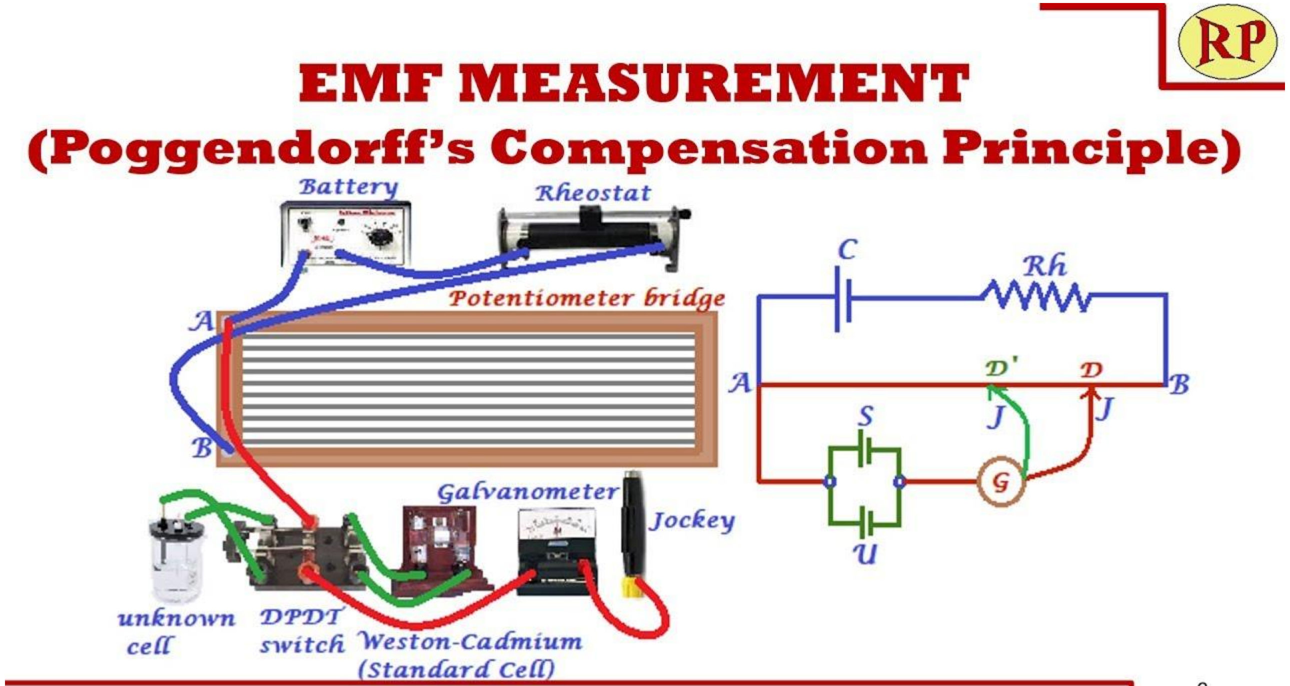
Kada je $\varepsilon = \varepsilon^0$ **?**

Kompenzaciona metoda merenja EMS

- Instrument sa visokom ulaznom impedansom
- **Kompenzaciona metoda merenja EMS**

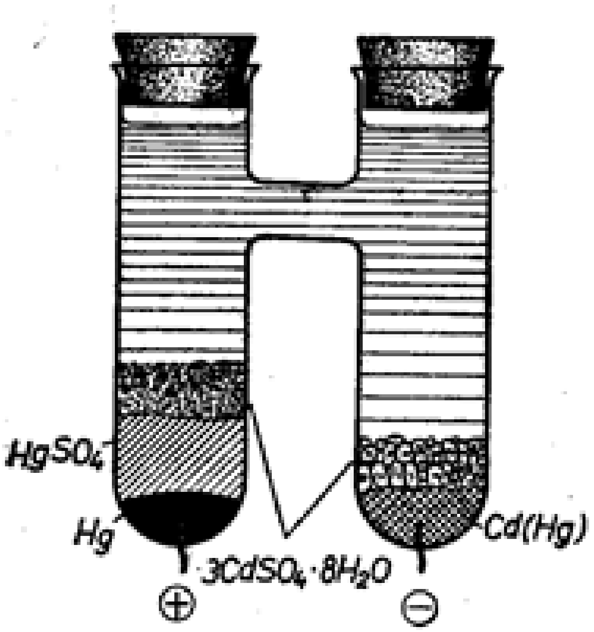


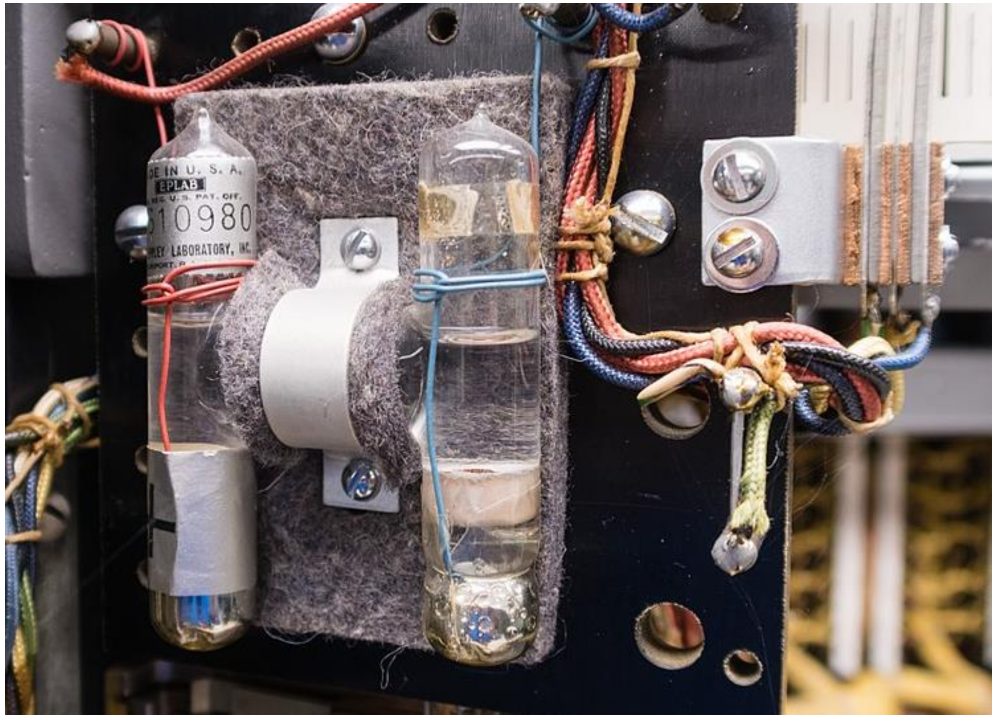
$$\frac{\overline{AC_N}}{\overline{AC_x}} = \frac{\varepsilon_N}{\varepsilon_x}$$



Etalon elektromotorne sile

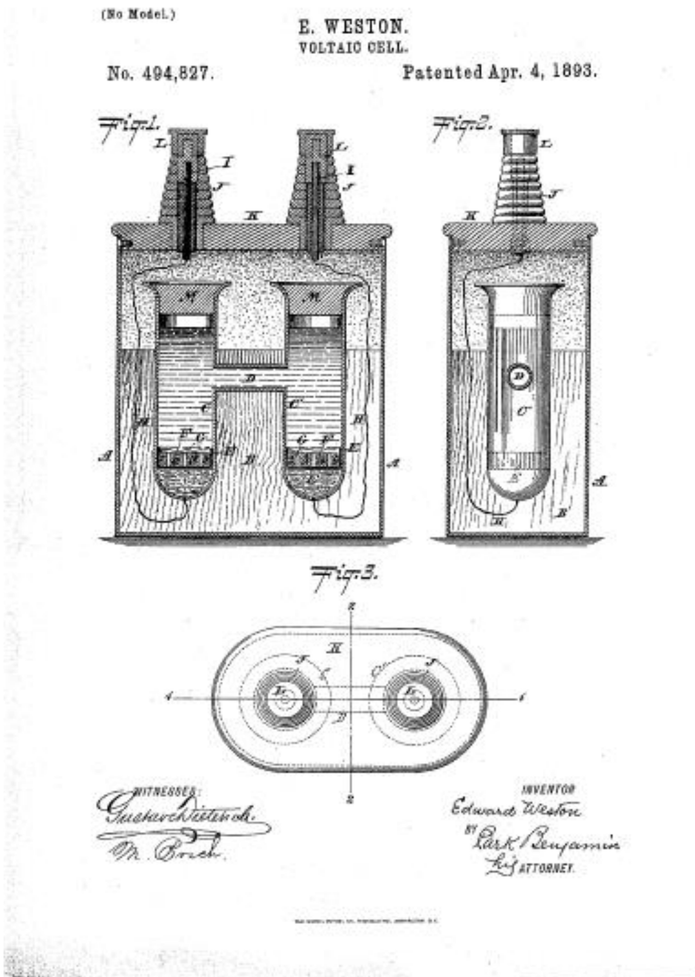
- Vestonov element

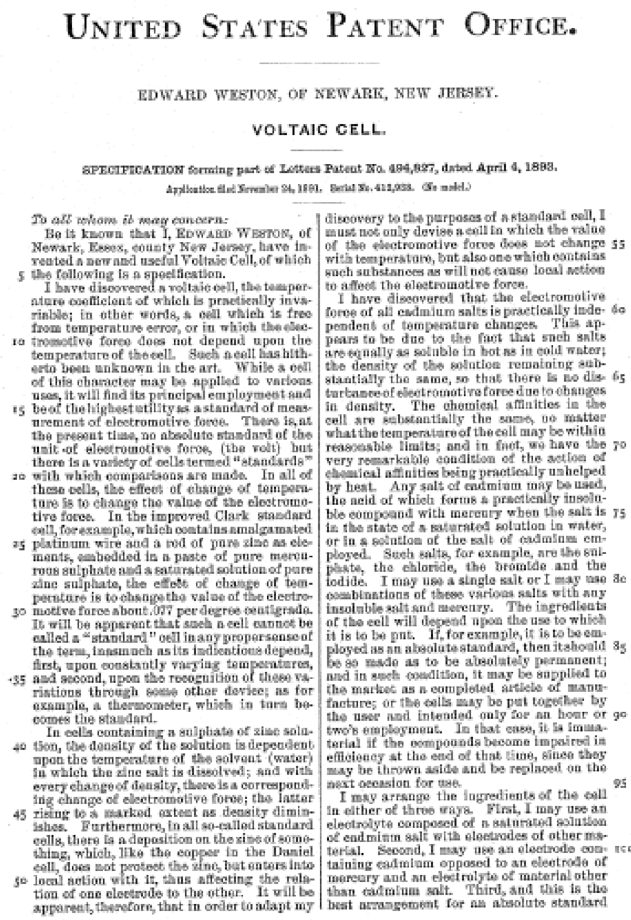




$$\mathbf{Cd(Hg)\,|\,3CdSO_4\cdot 8H_2O,\ H_2O\,|\,Hg_2SO_4\,|\,Hg}$$

Etalon elektromotorne sile



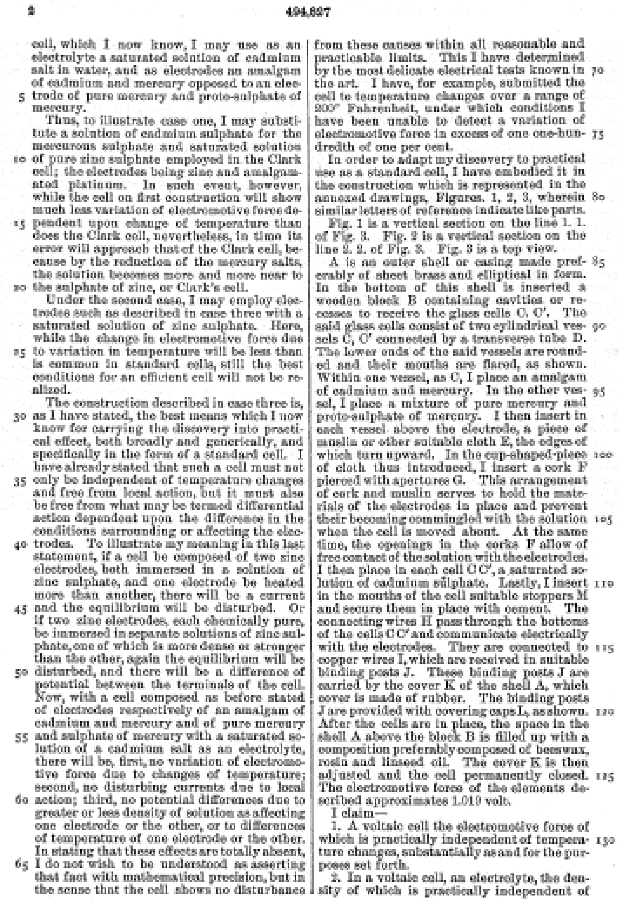


UNITED STATES PATENT OFFICE.

EDWARD WESTON, OF NEWARK, NEW JERSEY.

VOLTAIC CELL.

SPECIFICATION forming part of Letters Patent No. 494,827, dated April 4, 1893.



2 494,827

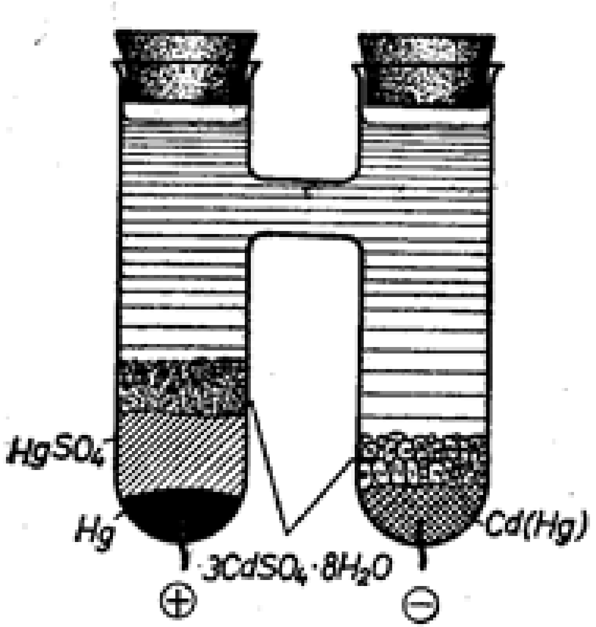
https://patents.google.com/patent/US494827

Etalon elektromotorne sile

- Vestonov element

$Cd(Hg)\,|\,3CdSO_4\cdot 8H_2O,\ H_2O\,|\,Hg_2SO_4\,|\,Hg$

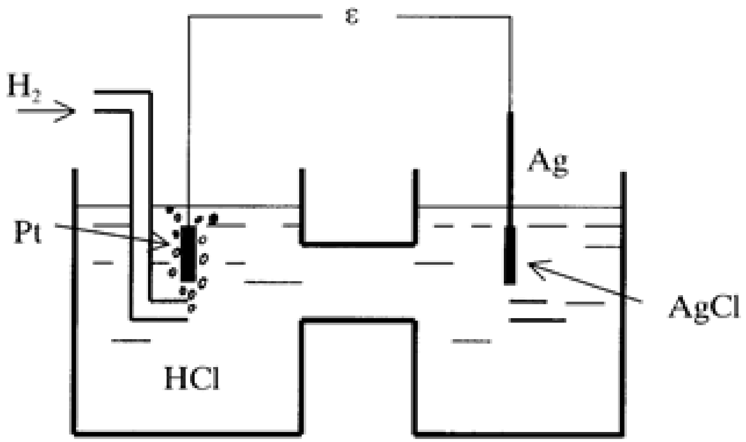
Cd(Hg) + Hg2SO4 → 2Hg + CdSO4



$$\varepsilon = \varepsilon^0 - \frac{RT}{2F}\ln\frac{a_{Hg}^2 \cdot a_{CdSO_4}}{a_{Cd(Hg)} \cdot a_{Hg_2SO_4}}$$

$$\varepsilon_t = 1{,}018300 - 4{,}06\cdot 10^{-5}(t - 20) - 9{,}5\cdot 10^{-7}(t - 20)^2 - 1\cdot 10^{-8}(t - 20)^3$$

Određivanje standardne elektromotorne sile i koeficijenata aktivnosti (vežba na III kolokvijumu)



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

⬇

$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

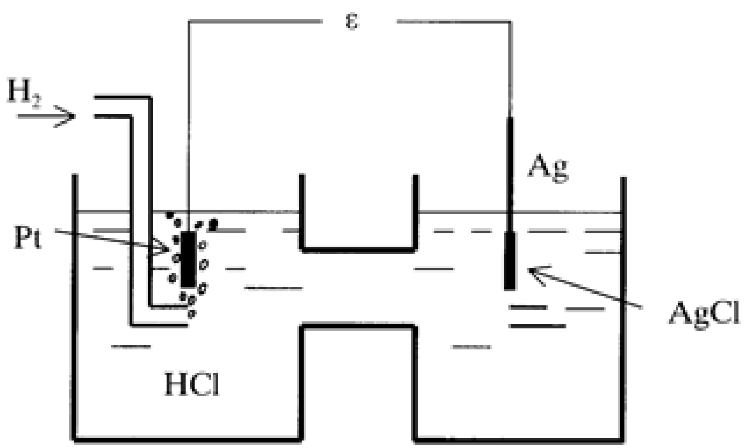
$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln\frac{a_{H^+}\cdot a_{Cl^-}\cdot a_{Ag}}{p_{H_2}^{1/2}\, a_{AgCl}}$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln a_{H^+}\cdot a_{Cl^-}$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln(m_{H^+}\gamma_{H^+} m_{Cl^-}\gamma_{Cl^-})$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln m^2\gamma_\pm^2$$

Određivanje standardne elektromotorne sile i koeficijenata aktivnosti (vežba na III kolokvijumu)



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

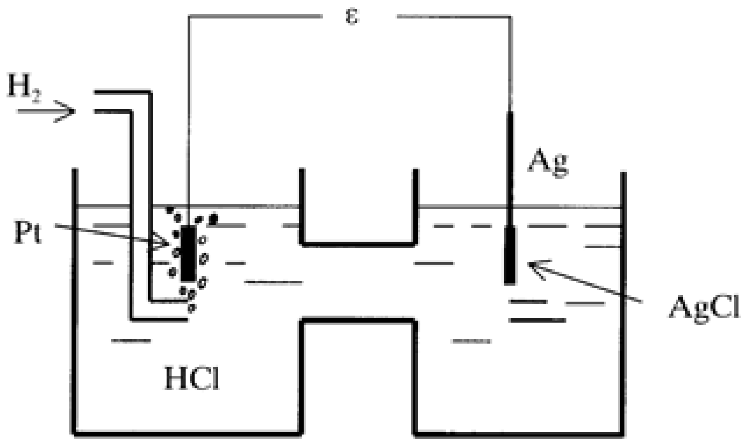
$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln m^2 - \frac{RT}{F}\ln \gamma_\pm^2$$

$$\varepsilon + \frac{RT}{F}\ln m^2 = \varepsilon^0 - \frac{RT}{F}\ln \gamma_\pm^2$$

$$\boxed{\varepsilon + \frac{2RT}{F}\ln m = f(m)}$$

Određivanje standardne elektromotorne sile i koeficijenata aktivnosti (vežba na III kolokvijumu)



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

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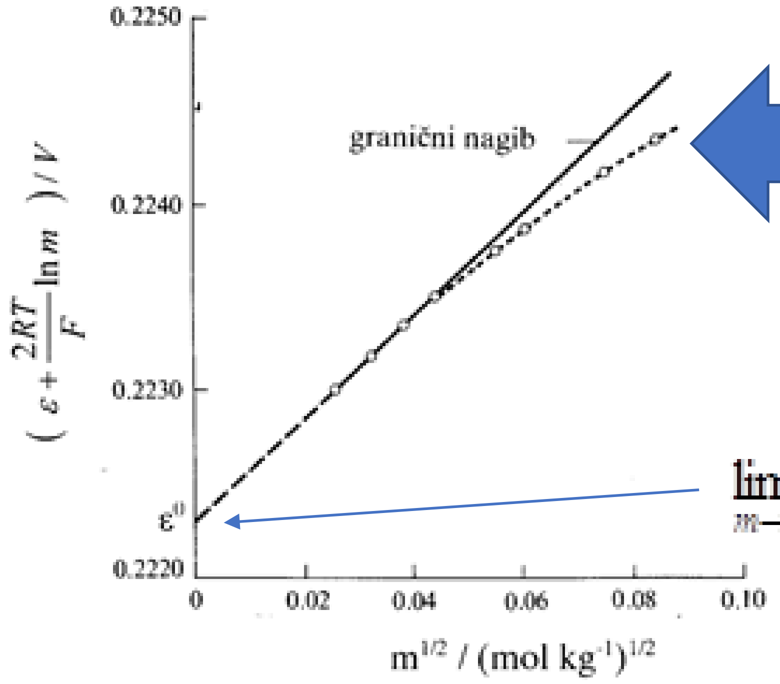
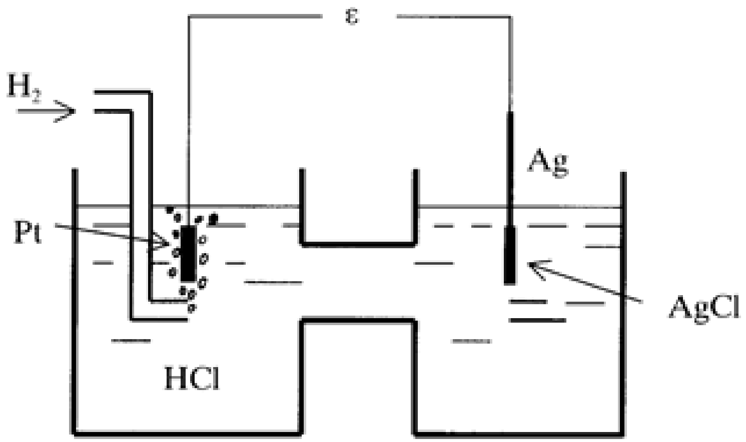
$$\varepsilon + \frac{2RT}{F}\ln m = f(m)$$



!!!!!!!

$$\lim_{m \to 0} \varepsilon + \frac{2RT}{F}\ln m = \varepsilon^0$$

Određivanje standardne elektromotorne sile i koeficijenata aktivnosti (vežba na III kolokvijumu)



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

$$\log \gamma_\pm = -0{,}509\sqrt{I} + BI$$

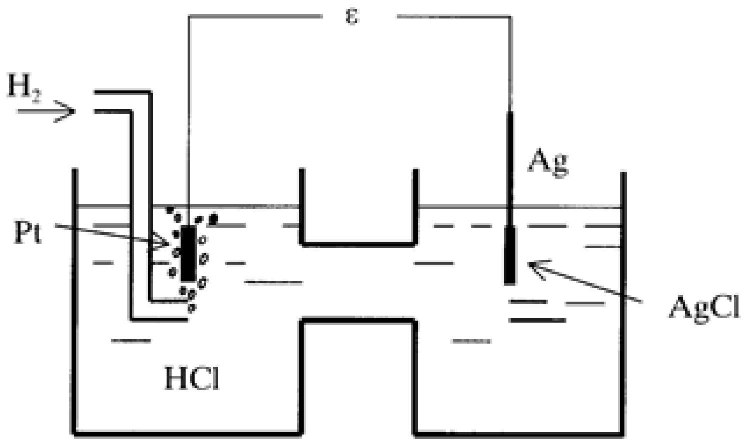
$$\log \gamma_\pm = -0{,}509\sqrt{m} + Bm$$

HCl (!!!!)

$$\varepsilon + \frac{2 \cdot 2{,}303RT}{F}\log m = \varepsilon^0 - \frac{2 \cdot 2{,}303}{F}RT \cdot \left(-0{,}509\sqrt{m} + Bm\right)$$

$$\varepsilon^* = \varepsilon + \frac{4{,}606}{F}RT\log m - \frac{2{,}34RT}{F}\sqrt{m} = \varepsilon^0 - \frac{4{,}606RTBm}{F}$$

Određivanje standardne elektromotorne sile i koeficijenata aktivnosti (vežba na III kolokvijumu)



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

$$\varepsilon^* = \varepsilon + \frac{4{,}606}{F}RT\log m - \frac{2{,}34RT}{F}\sqrt{m} = \varepsilon^0 - \frac{4{,}606RTBm}{F}$$

Nagib → B

$$\log\gamma_\pm = -0{,}509\sqrt{I} + BI$$

$m \rightarrow 0$

$$\varepsilon^0$$

Određivanje standardne elektromotorne sile galvanskog elementa sa alkalnim elementima kao reaktantima

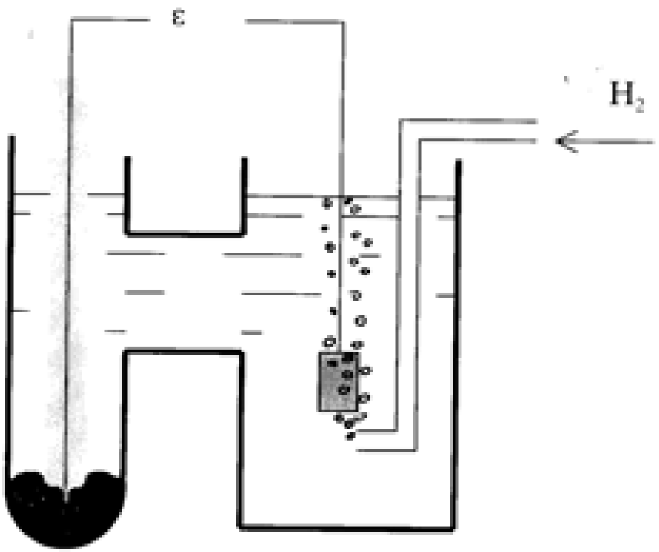
Ali alkalni elementi nisu stabilni u vodi

Pa nemoj da koristiš vodu

Ali nemam aprotični rastvarač

Koristi amalgam

Određivanje standardne elektromotorne sile galvanskog elementa sa alkalnim elementima kao reaktantima



$$Na(Hg) \Leftrightarrow Na^{+} + e \qquad H^{+} = e \Leftrightarrow \frac{1}{2}H_2$$

$$Na(Hg) + HCl \rightarrow NaCl + \frac{1}{2}H_2$$

Sastav elektrolita!

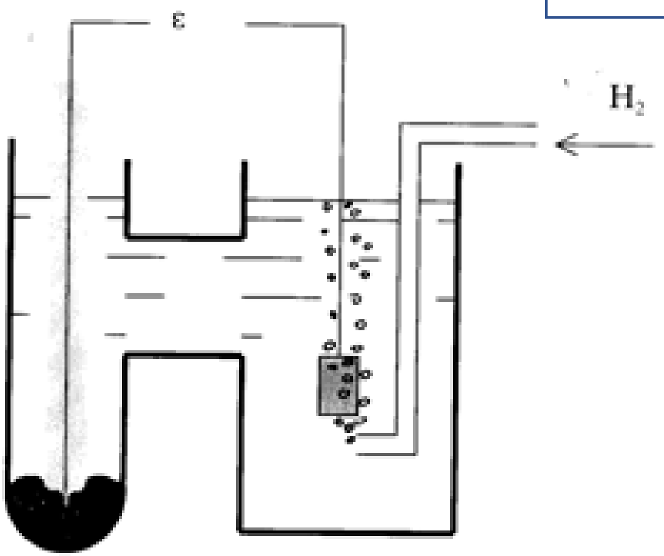
$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln\frac{a_{NaCl}\cdot p_{H_2}^{1/2}}{a_{HCl}\cdot a_{Na(Hg)}}$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln\frac{a_{NaCl}}{a_{HCl}\cdot a_{Na(Hg)}}$$

Određivanje standardne elektromotorne sile galvanskog elementa sa alkalnim elementima kao reaktantima

$$\varepsilon + \frac{2RT}{F}\ln m_{NaCl} - \frac{2RT}{F}\ln m_{HCl} = \varepsilon^0 + \frac{RT}{F}\ln a_{Na(Hg)} - \frac{2RT}{F}\ln \gamma_{\pm,NaCl} + \frac{2RT}{F}\ln \gamma_{\pm,HCl}$$

$$= f(I)$$



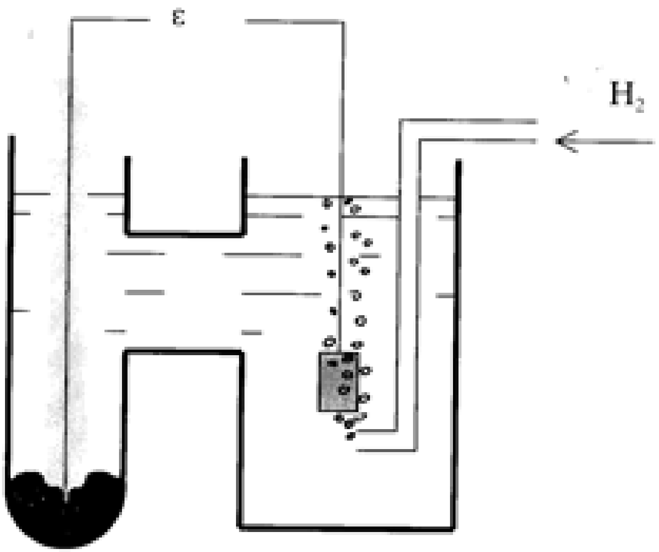
$$Na(Hg) \Leftrightarrow Na^+ + e \qquad H^+ = e \Leftrightarrow \frac{1}{2}H_2$$

$I \rightarrow 0$

$$\varepsilon^0 + \frac{RT}{F}\ln a_{Na(Hg)} - \frac{2RT}{F}\ln \gamma_{\pm,NaCl} + \frac{2RT}{F}\ln \gamma_{\pm,HCl}$$

$$Na(Hg) + HCl \rightarrow NaCl + \frac{1}{2}H_2$$

Određivanje standardne elektromotorne sile galvanskog elementa sa alkalnim elementima kao reaktantima

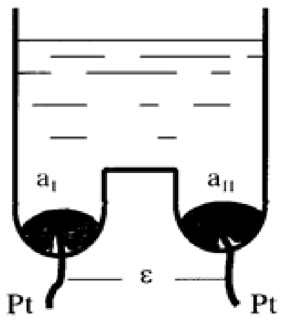


$$\varepsilon^0 + \frac{RT}{F}\ln a_{Na(Hg)}$$

Predavanje 8

$$Na(Hg) \Leftrightarrow Na^+ + e \qquad H^+ = e \Leftrightarrow \frac{1}{2}H_2$$

$$Na(Hg) + HCl \rightarrow NaCl + \frac{1}{2}H_2$$

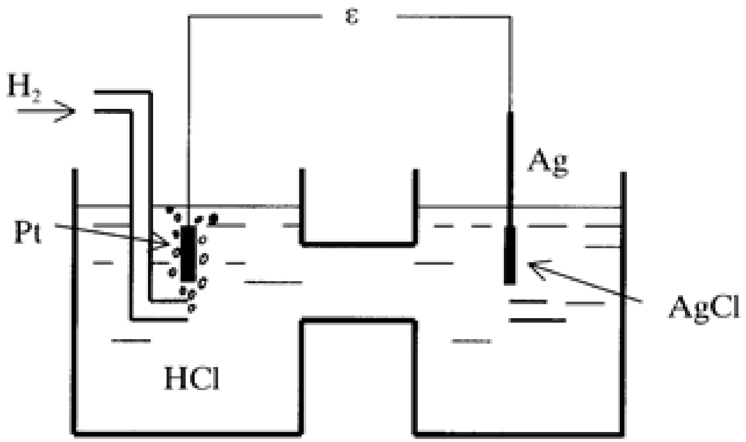


$$\varepsilon = -\frac{RT}{nF}\ln a_{M(Hg)}$$

Told you so!

Ako je jedna elektroda čist metal

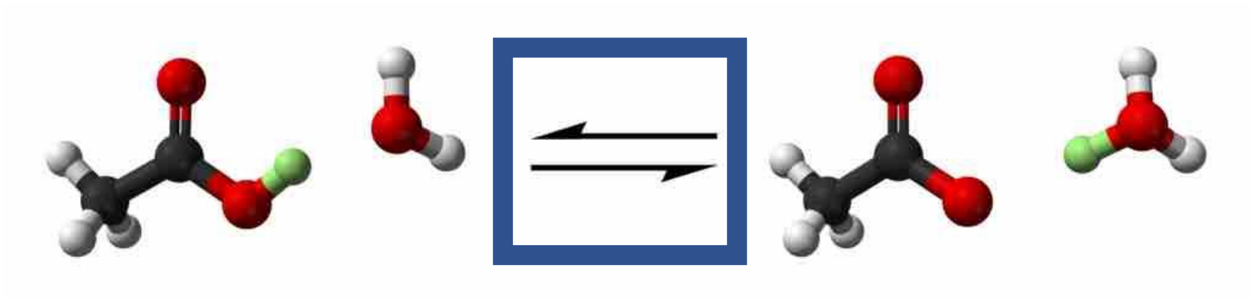
Određivanje konstante disocijacije slabe kiseline na osnovu merenja EMS



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

H⁺ je iz slabe kiseline!



Sastav elektrolita!

Pt, H_2 (1 atm) | HA(m_1), NaA(m_2), NaCl(m_3) | AgCl, Ag

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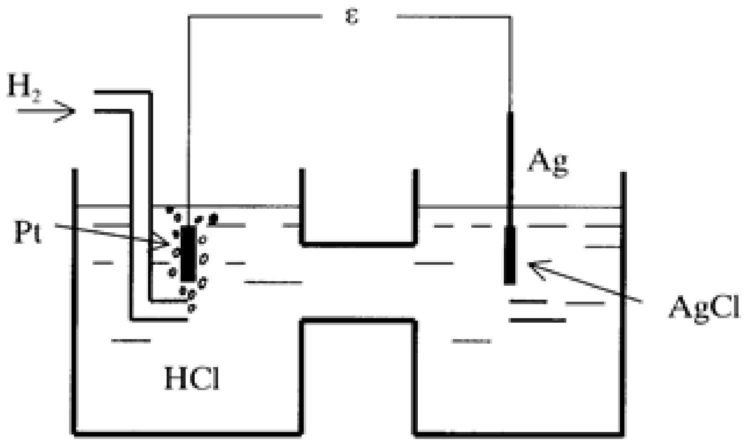

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Sastav elektrolita!

Pt, H_2 (1 atm) | HA(m_1), NaA(m_2), NaCl(m_3) | AgCl, Ag

Izvor protona za anodnu reakciju

Zajednički anjon **Kontrola disocijacije**

Izvor Cl^- za katodnu reakciju

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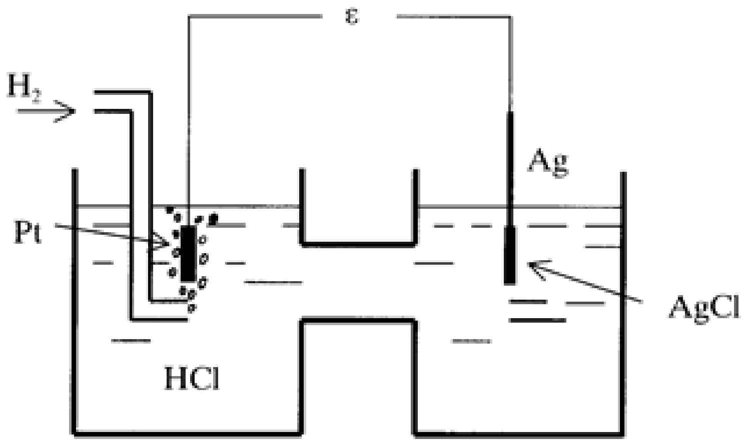


$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln a_{H^+} \cdot a_{Cl^-}$$

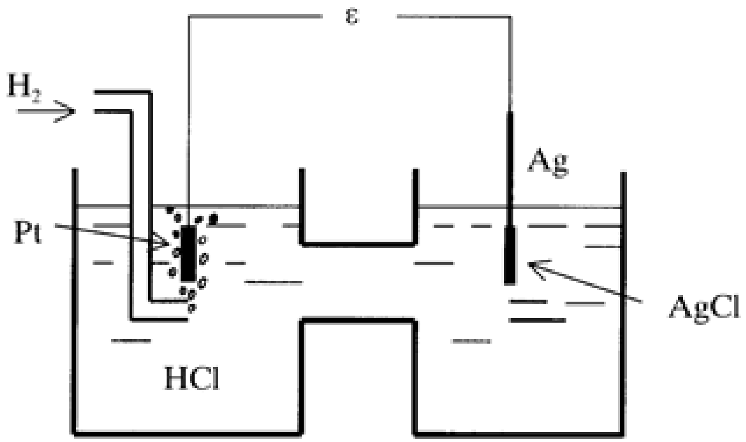
$$K = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \Rightarrow a_{H^+} = \frac{K \cdot a_{HA}}{a_{A^-}}$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln \frac{a_{HA} \cdot a_{Cl^-}}{a_{A^-}} \cdot K$$

$$a = m\gamma$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln \frac{m_{HA} \cdot m_{Cl^-}}{m_{A^-}} - \frac{RT}{F}\ln \frac{\gamma_{HA} \cdot \gamma_{Cl^-}}{\gamma_{A^-}} - \frac{RT}{F}\ln K$$

Određivanje konstante disocijacije slabe kiseline na osnovu merenja EMS



$$\frac{1}{2}H_2 \rightarrow H^+ + e \qquad AgCl + e \rightarrow Ag + Cl^-$$

$$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{F}\ln\frac{m_{HA}\cdot m_{Cl^-}}{m_{A^-}} - \frac{RT}{F}\ln\frac{\gamma_{HA}\cdot\gamma_{Cl^-}}{\gamma_{A^-}} - \frac{RT}{F}\ln K$$

$$\frac{\varepsilon-\varepsilon^0}{0{,}0591} + \log\frac{m_{HA}\cdot m_{Cl^-}}{m_{A^-}} = -\log\frac{\gamma_{HA}\cdot\gamma_{Cl^-}}{\gamma_{A^-}} - \log K$$

$$\frac{\varepsilon-\varepsilon^0}{0{,}0591} + \log\frac{m_{HA}\cdot m_{Cl^-}}{m_{A^-}} = f(I)$$

$I \rightarrow 0$

$$-\log K$$

Korisni linkovi

- **Proučite uputstvo za vežbu (stranica predmeta!)**
- http://electro.chem.elte.hu:5080/Laboranyag/Chemistry_BSc_English_Group/BLOCK_09/Electromotive_force_2014.pdf
- https://www.sciencedirect.com/topics/chemistry/electromotive-force
- RAD O MERENJU EMS IZ 1883: https://www.jstor.org/stable/pdf/982459.pdf