2. laskuharjoitus, ratkaisut

(1)

$$v_i = u_i E \qquad u_i = \frac{z_i D_i F}{RT}$$

$$D_i = 1.3\cdot 10^{-5}\ cm^2/s = 1.3\cdot 10^{-9}\ m^2/s$$

$$E = 0.5\ V/cm = 50\ V/m$$

$$v_i = \frac{1.3\cdot 10^{-9}\ m^2/s \cdot 96500\ As/mol}{8.314\cdot 298\ VAs/mol}\cdot 50\ V/m \approx \underline{\underline{2.5\ \mu m/s}}$$

Huom. $J = VAs$

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(2)

$$j = F\sum_i z_i J_i = F\left(-\sum_i z_i D_i \nabla c_i - \frac{F}{RT}\nabla\phi \sum_i z_i^2 D_i c_i + v\sum_i z_i c_i\right)$$

Koska $\sum_i z_i c_i = 0$ elektroneutraaliuden vuoksi, virta ei riipu konvektiosta. □

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(3)

$$-\frac{j}{F} = \sum_i z_i D_i \nabla c_i + \frac{F}{RT}\nabla\phi \sum_i z_i^2 D_i c_i$$

$$\nabla\phi = -\frac{j}{\frac{F^2}{RT}\sum_i z_i^2 D_i c_i} - \frac{\sum_i z_i D_i c_i \nabla \ln c_i}{\sum z_i^2 D_i c_i}\frac{RT}{F}$$

$$= -\frac{j}{\varkappa} - \frac{RT}{F}\sum_i\left(\frac{t_i}{z_i}\right)\nabla \ln c_i = -\frac{j}{\varkappa} - \frac{1}{F}\sum_i\left(\frac{t_i}{z_i}\right)\nabla\mu_i$$

$$\varkappa = \frac{F^2}{RT}\sum_i z_i^2 D_i c_i = \text{liuoksen johtokyky}$$

$$t_i = \frac{z_i^2 D_i c_i}{\sum_k z_k^2 D_k c_k} = \text{ionin kuljetusluku} = \frac{\lambda_i c_i}{\varkappa}$$

(4) Ratkaisu ei ole yleinen, mutta demonstroidaan seuraavasti:

On mitattu Λ_{NaCl}, Λ_{CaCl_2}, $\Lambda_{Na_2SO_4}$ ja Λ_{CaSO_4}

"1" = Na^+, "2" = Ca^{2+}, "3" = Cl^-, "4" = SO_4^{2-}

Tehdään matriisiyhtälö

$$\begin{bmatrix} \Lambda_{13} \\ \Lambda_{23} \\ \Lambda_{14} \\ \Lambda_{24} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 2 & 0 \\ 2 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \lambda_4 \end{bmatrix}$$

$$L = A \cdot l$$

Ratkaisu olisi $A^{-1}L = l$, mutta:

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```
>> A=[1 0 1 0;0 1 2 0;2 0 0 1;0 1 0 1]

A =

     1     0     1     0
     0     1     2     0
     2     0     0     1
     0     1     0     1

>> B=inv(A)
Warning: Matrix is singular to working precision.

B =

   Inf   Inf   Inf   Inf
   Inf   Inf   Inf   Inf
   Inf   Inf   Inf   Inf
   Inf   Inf   Inf   Inf
```

Käänteismatriisia ei ole olemassa

$\Rightarrow$ väite □