Modelling of multicomponent ion exchange in lithium-ion battery recycling

Tobias Wesselborg, Dr. Sami Virolainen and Prof. Tuomo Sainio

Tobias Wesselborg

LUT University, Finland

tobias.wesselborg@lut.fi





Background





Background



 Literature lacks in LIB metal equilibrium data at higher concentrations and acidities





Methodology, experimentals, theory on modelling of ion exchange



Methodology and experimentals



- Batch equilibrium experiments at 22°C and 60°C
- Resin phase: Lewatit® TP 260 in protonated form, functional group: AMPA
- Aqueous phase: LIB metals at varied concentrations in sulfate media
- Adjusted pH values: 0, 1 and 1.8
- Intermittent pH adjustment with NaOH and H₂SO₄ until pH is constant
- Digestion of dried loaded resin
- Analytics: ICP-MS and AAS



Example: Experimental results for the ternary system Cu+Na+H



Three isotherms for uptake of Cu at a constant pH can be identified The metal uptake increases with the increase of pH and temperature. The effect of temperature is enhanced with higher pH values.

Metal uptake is enhanced with increased pH and increased temperature





Example: Experimental results for the ternary system Cu+Na+H



Metal uptake is enhanced with increased pH and increased temperature



Tobias Wesselborg (Tobias.Wesselborg@lut.fi), Sami Virolainen, Tuomo Sainio

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Modelling methodology

- Idea: Model each LIB metal separately and use determined model parameters to model the multi metal solution (LIBWL)
 - Each system is a ternary system and consists of three cation species (one LIB metal, Na and H)
 - One binary cation system: Na and H to determine model parameters for Na
- Assumptions:
 - Model parameters for each cation species are independent
 - Proton concentration via pH measurement: $\alpha(H) \approx c(H)$
 - Only phosphonic acid group participates in IX, i.e. amine group is always protonated due to low pH and calculation of $q_{H,exp}$ via mole balance

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OF: minimizing sum of squared error (i.e. method of least squares)

Theory on modelling of ion exchange (IX)

- Characteristics of IX in comparison to physical adsorption:
 - Charge balance (i.e. electroneutrality applies):
 - All sites are permanently occupied:
 - Competition between ions, i.e. the system has at least two cations or anions
- Thus, physical adsorption isotherm models <u>cannot</u> be applied.

• Freundlich
$$q_i = Kc_i^{\frac{1}{n}}$$
 and Langmuir $q_i = \frac{q_{max}K_ic_i}{1+K_ic_i}$

• Competitive Langmuir
$$q_i = \frac{q_{max}K_ic_i}{1+\sum K_jc_j}$$



$$\Theta_i = \frac{|z_i| \cdot q_i}{|z_r| \cdot q_{max}}$$
$$\sum_i |z_j| q_j = |z_r| q_{max}$$



Mass Action Law (MAL)

- Stoichiometric equilibrium of an ion exchange reaction:
 - E.g. $Cu^{2+} + 2\underline{H}^+ \rightleftharpoons \underline{Cu}^{2+} + 2H^+$

• MAL:
$$K_{CuH} = \left(\frac{\alpha(\underline{Cu})}{\alpha(Cu)}\right)^1 \cdot \left(\frac{\alpha(H)}{\alpha(\underline{H})}\right)^2$$

• Literature also lacks in thermodynamic data to describe nonidealities of resin and aqueous phase.

• Simplification:
$$K_{CuH} = \left(\frac{c(\underline{Cu})}{c(Cu)}\right)^1 \cdot \left(\frac{c(H)}{c(\underline{H})}\right)^2 = \left(\frac{q(Cu)}{c(Cu)}\right)^1 \cdot \left(\frac{c(H)}{q(H)}\right)^2$$

Please note:

After simplification, K_{CuH} does not represent the thermodynamic equilibrium constant; K_{CuH} is the selectivity coefficient.

• Fitted model parameter: K_{CuH}





Non Ideal Competitive Adsorption isotherm model for IX

- Physical adsorption model rewritten for IX
- NICA-characteristics^[1]:
 - Explicit model
 - Affinity constant $K_i \neq f(pH)$
 - Nonideality is considered
 - $-h_i$ is an ion specific non-ideality parameter (0< $h_i \le 1$)
 - *p* describes the adsorption site heterogeneity

• NICA:
$$q_i = \Theta_{i,t} \cdot \frac{h_i}{h_H} \cdot q_{max,H}$$

with
$$\Theta_{i,t} = \frac{(K_i c_i)^{h_i}}{\sum_i (K_i c_i)^{h_i}} \cdot \frac{\left[\sum_i (K_i c_i)^{h_i}\right]^p}{1 + \left[\sum_i (K_i c_i)^{h_i}\right]^p}$$

IX characteristics are applied:

 $\sum_{j} |z_j| q_j = |z_r| q_{max}$ and $\Theta_i = \frac{|z_i| \cdot q_i}{|z_r| \cdot q_{max}}$

$$q_i = |z_r| q_{max} \frac{h_i (K_i c_i)^{h_i}}{\sum |z_j| h_j (K_j c_j)^{h_j}}$$

Fitted model parameters: K_i, h_i



^[1] D.G. Kinniburgh et al. / Colloids Surfaces A: Physicochem. Eng. Aspects 151 (1999) 147-166

• Per definition: $\log_{10} K_H = 0$ and $h_H = 1$

Ideal Competitive Ion Exchange Model

- Equation is obtained by setting $h_i = 1$ in NICA-IX model
 - NICA-IX: $q_i = |z_r| q_{max} \frac{h_i (K_i c_i)^{h_i}}{\sum |z_j| h_j (K_j c_j)^{h_j}}$
- Ideal Competitive Ion Exchange Model: $q_i = \frac{|z_r|q_{max}K_ic_i}{\sum |z_j|K_jc_j}$
- Fitted model parameter: K_i





Experimental and modelling results using MAL, ideal competitive ion exchange and NICA-IX models with a fixed set of model parameters



Results for MAL, ideal competitive ion exchange model and NICA-IX at T=22°C



Please note:



Calculated results are not presented as solid lines because the metal (Li) uptake also depends on the pH and Na concentration in the aqueous phase. Tobias Wesselborg (Tobias.Wesselborg@lut.fi), Sami Virolainen, Tuomo Sainio

- Exemplarily, the experimental and modeled results for Li at 22°C are shown.
 - Due to brevity, only the LIB metal uptake is shown. Corresponding uptakes of Na and H are not shown for the ternary systems (LIB metal + Na + H).
- The experimental data is not well explained by the models.
 - Deviations between experimental and modeled data are highlighted exemplarily.
 - The models cannot explain the effect of the proton concentration with a fixed set of model parameters when the acid concentration changes 10 or 100 times, i.e. 1-2 steps on the pH scale.



Results for MAL, ideal competitive ion exchange model and NICA-IX at T=22°C



Please note:



Calculated results are not presented as solid lines because the metal (Mn) uptake also depends on the pH and Na concentration in the aqueous phase. Tobias Wesselborg (Tobias.Wesselborg@lut.fi), Sami Virolainen, Tuomo Sainio

- Exemplarily, the experimental and modeled results for Mn at 22°C are shown.
 - Due to brevity, only the LIB metal uptake is shown. Corresponding uptakes of Na and H are not shown for the ternary systems (LIB metal + Na + H).
- The experimental data is not well explained by the models.
 - Deviations between experimental and modeled data are highlighted exemplarily.
 - The models cannot explain the effect of the proton concentration with a fixed set of model parameters when the acid concentration changes 10 or 100 times, i.e. 1-2 steps on the pH scale.



Results for MAL, ideal competitive ion exchange model and NICA-IX at T=22°C



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 The experimental data is not well explained with a fixed set of model parameters, differences are highlighted for Li and Mn exemplarily.



Results for MAL, ideal competitive ion exchange model and NICA-IX at T=60°C





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Modelling results using NICA-IX with a linear correlation of $log_{10} K_i$ and pH



An approach, how to model large changes in acid concentration

 <u>Observation</u>: At a given pH, the explicit NICA-IX model correlates well with the experimental data

• NICA-IX:
$$q_i = |z_r| q_{max} \frac{h_i (K_i c_i)^{h_i}}{\sum |z_j| h_j (K_j c_j)^{h_j}}$$

- <u>Idea:</u> linear correlation for log K_i and pH
 - $\log_{10} K_i = a_i pH + b_i$
- Fitted model parameters: a_i, b_i and h_i



The upper graph shows the experimentally measured uptake of Ni at 60°C and the modeled uptake using the NICA-IX model with a fixed set of model parameters. **Deviation between** experimental and modeled value are highlighted. The lower plot shows the experimental of Ni at 60°C and modeled uptake using NICA-IX with a linear correlation for the affinity constant and corresponding pH value.



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Example: Comparison of NICA-IX without and with correlation for log K at T=60°C





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Example: Comparison of NICA-IX without and with correlation for log K at T=60°C



Implementing a linear correlation for $\log_{10} K_i$ significantly improves the fit







Results for system Na+H using NICA-IX with log K_i = f(pH, T)

First and second column show the experimentally measured and modeled uptakes of Na and H, respectively. First and second row show the experimentally measured and modeled uptake of cation species at 22°C and 60°C. respectively.



 Good agreement between the experimentally measured and modelled equilibrium data for the binary system (cation species: Na⁺, H⁺) is achieved.



Results for system Li+Na+H using NICA-IX with log $K_i = f(pH, T)$



Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Ni²⁺, Na⁺, H⁺) is achieved. LUT University

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Results for system Ni+Na+H using NICA-IX with log $K_i = f(pH, T)$

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Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Ni²⁺, Na⁺, H⁺) is achieved. LUT University

Results for system Co+Na+H using NICA-IX with log K_i = f(pH, T)



Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Co²⁺, Na⁺, H⁺) is achieved. LUT University

Tobias Wesselborg (Tobias.Wesselborg@lut.fi), Sami Virolainen, Tuomo Sainio



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Results for system Cu+Na+H using NICA-IX with log $K_i = f(pH, T)$

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Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Cu²⁺, Na⁺, H⁺) is achieved. LUT University

Results for system Mn+Na+H using NICA-IX with log $K_i = f(pH, T)$



Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Mn²⁺, Na⁺, H⁺) is achieved. LUT University

Tobias Wesselborg (Tobias.Wesselborg@lut.fi), Sami Virolainen, Tuomo Sainio



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Results for system AI+Na+H using NICA-IX with log K_i = f(pH, T)



Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Al³⁺, Na⁺, H⁺) is achieved. LUT University

Tobias Wesselborg (Tobias.Wesselborg@lut.fi), Sami Virolainen, Tuomo Sainio



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Results for system Fe+Na+H using NICA-IX with log K_i = f(pH, T)



Good agreement between the experimentally measured and modelled equilibrium data for the ternary system (cation species: Fe³⁺, Na⁺, H⁺) is achieved.



Results for modelling of multicomponent (LIBWL) IX equilibria with nine cations (H, Na, Li, Co, Ni, Cu, Mn, Fe, Al)



Notes on the multicomponent equilibrium (LIBWL) measurements and modelling

- Experimental procedure for LIBWL equilibrium data like in single equilibrium metal measurements
 - Obtained aqueous phase equilibrium concentration is used to calculate resin phase concentration
 - Experimentally measured solid phase composition is compared to the modeled one
 - pH range was 0 1.8 including values between 0 and 1 as well as 1 and 1.8 to see if model calculation is correct

• LIBWL:		Al	Со	Cu	Fe	Li	Mn	Ni
	c [g/L]	1.5	16.8	2.1	0.8	2.5	2.1	2.0

- NICA-IX with log $K_i = f(pH, T)$ is still an explicit model
 - Advantage: input values are concentrations of aqueous phase and corresponding resin phase concentration is calculated

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Results for modelling of multicomponent (LIBWL) IX equilibria using the gained model parameters at T=22°C

Chelating resin TP260 was contacted with synthetic LIBWL. Graph shows the experimentally measured and modeled uptake of cation species at 22°C.

Region for uptake of LIB metals is highlighted.



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The model and experimental data for synthetic LIBWL with nine cations correlate well.
Tobias Wesselborg (Tobias Wesselborg@lut.fl), Sami Virolainen, Tuomo Sainio

Results for modelling of multicomponent (LIBWL) IX equilibria using the gained model parameters at T=60°C

Chelating resin TP260 was contacted with synthetic LIBWL. Graph shows the experimentally measured and modeled uptake of cation species at 60°C.

Region for uptake of LIB metals is highlighted.



phase.

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 The model and experimental data for synthetic LIBWL with nine cations correlate well.

Summary, Conclusion and Outlook

- Equilibrium data for the chelating resin Lewatit® TP260 and LIB metals at higher concentrations and acidities was measured for three pH values at 22°C and 60°C
- MAL, ideal competitive ion exchange model and NICA-IX with a fixed set of parameters cannot explain the equilibrium data
- A semi-empirical model (NICA-IX with lin. correlation of log₁₀ K_i and pH) is suggested and explains the equilibrium data for the single metals well
- Calculated resin phase composition for a given liquid phase with nine cations (synthetic LIBWL) correlates well with the experimental data
- Data and model will help in process development of LIB recycling processes





Acknowledgement

- Financial support:
 - BATix, funded by Steel and Metal Producers' Fund



Teknologiateollisuuden 100-vuotissäätiö

- Supervisors and co-authors:
 - Prof. Tuomo Sainio
 - Dr. Sami Virolainen



