Echem Rnx. Engg. CL 611

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Characterization Methods

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Admin

- Extra Class:
  - Wednesday?
- Project weightage: 10% (5% bonus for extra efforts based on presentation)
- Project Timeline:
  - Project topic submission: 24th Oct 11.59 PM (Moodle) PPT Format
    - Project statement undertaken, objective, proposed work steps, novelty and difference from existing projects in COMSOL
    - How it is related to the course-work.
    - Distribution of the work and timelines. (not more than 2 slides per group).
  - Help :
    - Today after the class
    - Online session tomorrow (based on request)
  - Intermediate update: Help session will be organized.
  - Final submission: 10th Nov 11.59 PM
    - Presentation submission 10th Nov
    - 20 min presentation (timing flexible).

Quiz

Thursday Last 20 mins:

Quiz syllabus: Transport

You should be able to solve the following problem:

ILLUSTRATION 4.5

ILLUSTRATION 5.1

ILLUSTRATION 5.3

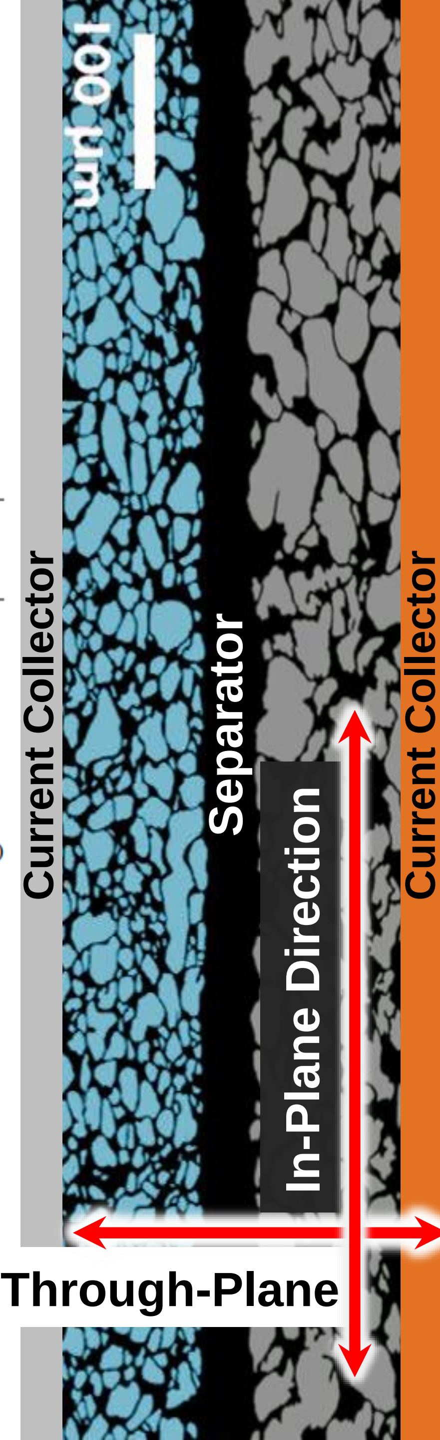
Characterization of Battery Systems

Non-invasive:
1. Rete tests
2. Pulse tests (DCIR)
3. Electrochemical Impedance spectroscopy
   - Transport resistance
   - Reaction kinetics, capacity fade expression

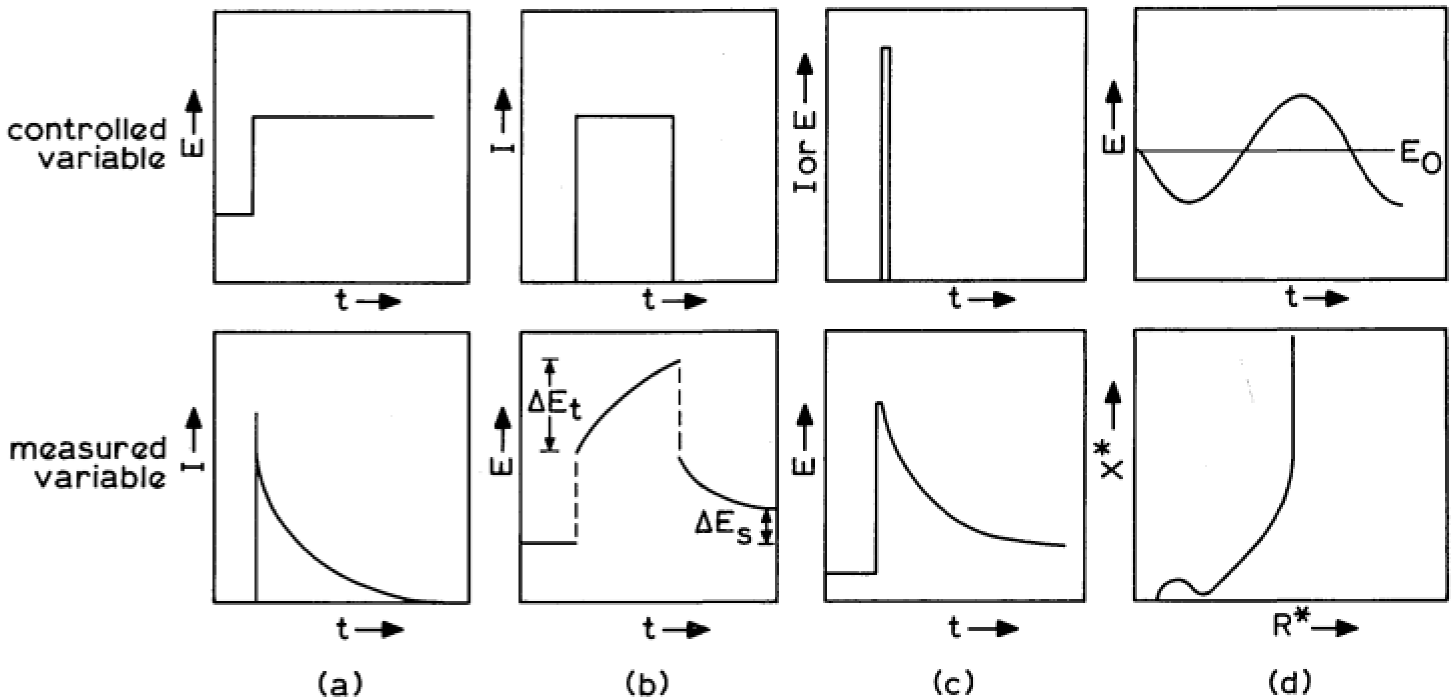
Invasive:
1. Geometric parameters
   Thicknesses, porosities, area, particle size and shape
2. Post-mortem analysis

Table V. List of parameters.

Symbol	Parameter	Positive Electrode[a]	Separator[a]	Negative Electrode[a]	Units
a_i	Particle Surface Area to Volume	354000		144720	m^2/m^3
Brugg	Bruggeman Coefficient	1.5[b]	1.5[b]	1.5[b]	
$c^s_{i,max}$	Maximum solid phase concentration	51554		30555	mol/m^3
$c^s_{i,0}$	Initial solid phase concentration	$c^s_{p,max} \times 0.95$		$c^s_{n,max} \times 0.105$	mol/m^3
c_0	Initial electrolyte concentration	1000	1000	1000	mol/m^3
D	Electrolyte diffusivity	7.5×10^{-10}	7.5×10^{-10}	7.5×10^{-10}	m^2/s
D^s_i	Solid Phase Diffusivity	1×10^{-14}		3.9×10^{-14}	m^2/s
F	Faraday's Constant		96487		C/mol
k_i	Reaction Rate constant	2.33×10^{-11}		5×10^{-10}	$m^{2.5}/(mol^{0.5}\ s)$
l_i	Region thickness	80×10^{-6}	25×10^{-6}	88×10^{-6}	m
$R_{p,i}$	Particle Radius	5×10^{-6}[b]		10×10^{-6}[b]	m
R	Gas Constant		8.314		J/mol/ K
T_{ref}	Temperature		298.15		K
t_+	Transference number		0.364		
$\varepsilon_{f,i}$	Filler fraction	0.025		0.0326	
ε_i	Porosity	0.385	0.724	0.485	
σ_i	Solid phase electronic conductivity	59		48.24	S/m
Ω	Partial molar volume	4.0815×10^{-6}[c]			m^3/mol
E	Young's modulus	15×10^{9}[d]			Pa
ν	Poisson's ratio	0.3[d]			



Schematic Illustration of 4 Echem. Methods



a potentiostatic; *b* galvanostatic; *c* potentiometric; *d* steady-state ac

1 **Schematic illustration of four electrochemical methods**

Weppner and Huggins: 1981

Literature Review

Weppner and Huggins: 1977

Determination of the Kinetic Parameters of Mixed-Conducting Electrodes and Application to the System Li_3Sb

W. Weppner and R. A. Huggins*
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

Weppner and Huggins: 1977

Electrochemical Investigation of the Chemical Diffusion, Partial Ionic Conductivities, and Other Kinetic Parameters in Li_3Sb and Li_3Bi

W. WEPPNER AND R. A. HUGGINS
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

Received March 5, 1977; in revised form April 29, 1977

Weppner and Huggins: 1979

Thermodynamic and Mass Transport Properties of "LiAl"

C. John Wen,* B. A. Boukamp,* and R. A. Huggins*
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305
and W. Weppner
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Germany

Weppner and Huggins: 1981

Use of electrochemical methods to determine chemical-diffusion coefficients in alloys: application to 'LiAl'

C. J. Wen, C. Ho, B. A. Boukamp, I. D. Raistrick, W. Weppner, and R. A. Huggins

Diffusion Coefficient

- What is diffusion coefficient
- What is the unit of diffusivity
- Various diffusion coefficients
  - Self diffusion coefficient
    - Using NMR D_{Self}
  - Tracer diffusion coefficient
    - Using tracer experiments ($\mathrm{D}_{\text{tracer}} = f D_{\text{Self}}$)
    - f relates to crystal structure 0.5-1
  - Chemical diffusion coefficient
    - Proportionality factor in Fick's law
    - $\widetilde{D} = \underbrace{\left(\frac{d \ln a}{d \ln y}\right)}_{\substack{\text{Thermo.} \\ \text{factor ?}}} D_{\text{Self}}$, this factor can be as large as 10^4
      - Where a is the activity of the mobile species A in $\mathrm{A}_y\mathrm{B}$ and y is the atomic ratio of component A to B;

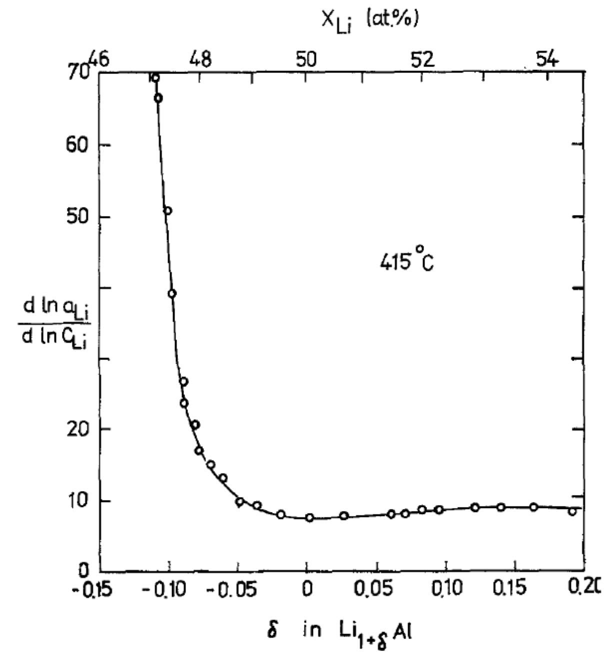
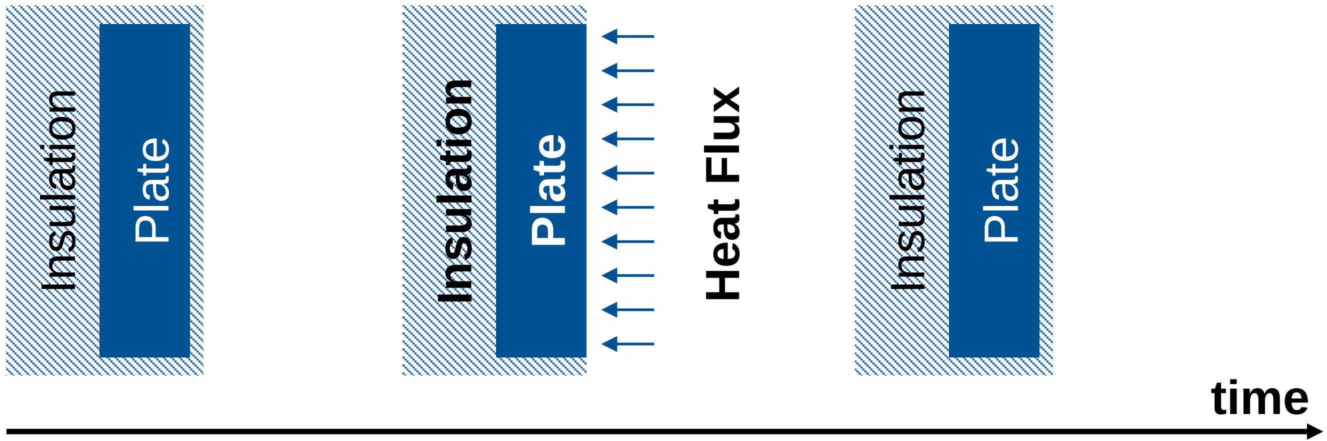


Fig. 5. Compositional variation of the enhancement factor within "LiAl" at 415°C.

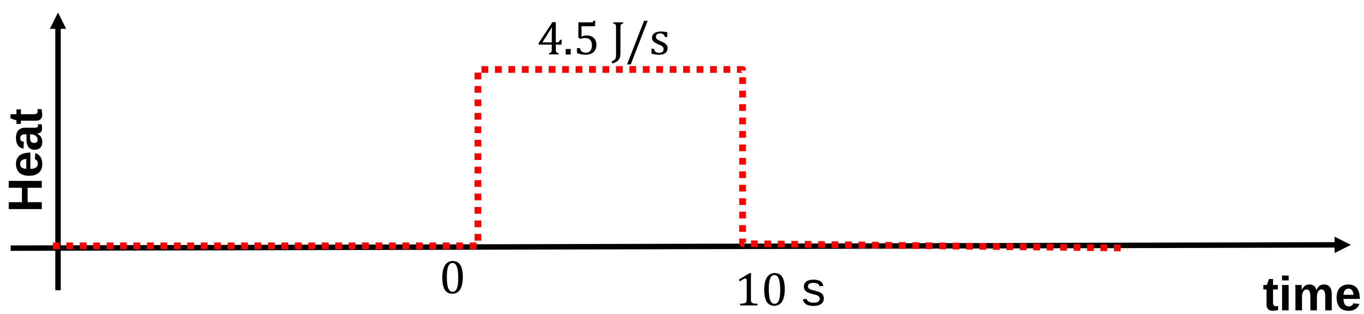
Weppner and Huggins: 1979 and 1981

Analogy: Heat Conductivity Exp.

Insulated iron plate
m =10 g
$T_0 = 25℃$
C_p =0.45 J/(g degC)

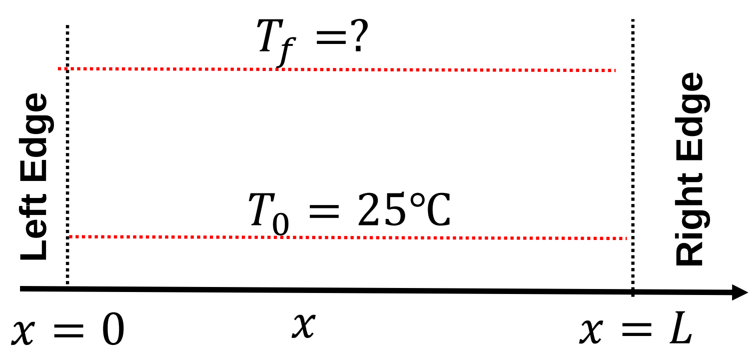


Constant heat
for 10 seconds

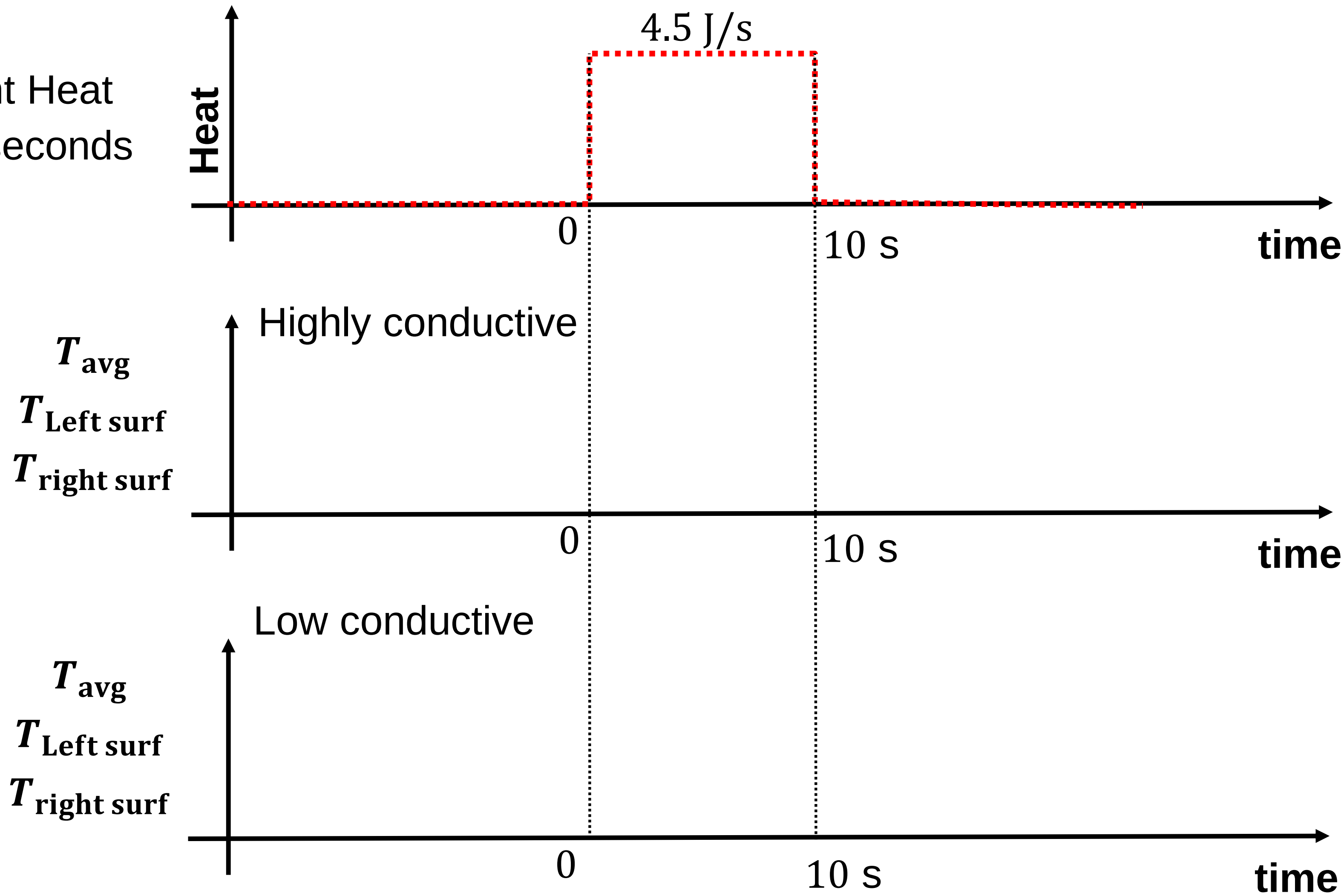


Plot the temperature profile inside the plate from left edge to right edge of metal plate.

- At t=0
- At t=infinity
- At intermediate time



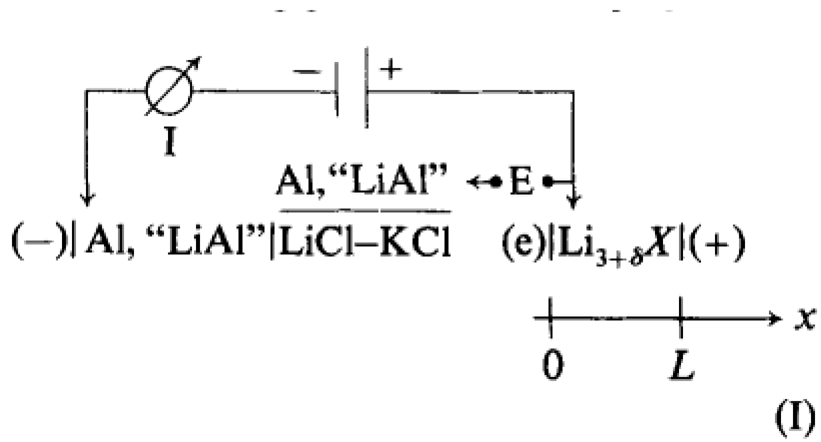
Constant Heat
For 10 seconds

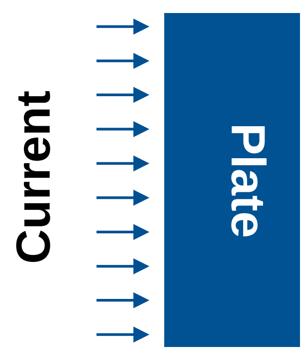


Experimental Setup

LiAl system: $> 400°C$

Al, 'LiAl' (s) | LiCl–KCl (eutectic) | 'LiAl' (s)





Weppner and Huggins: 1981

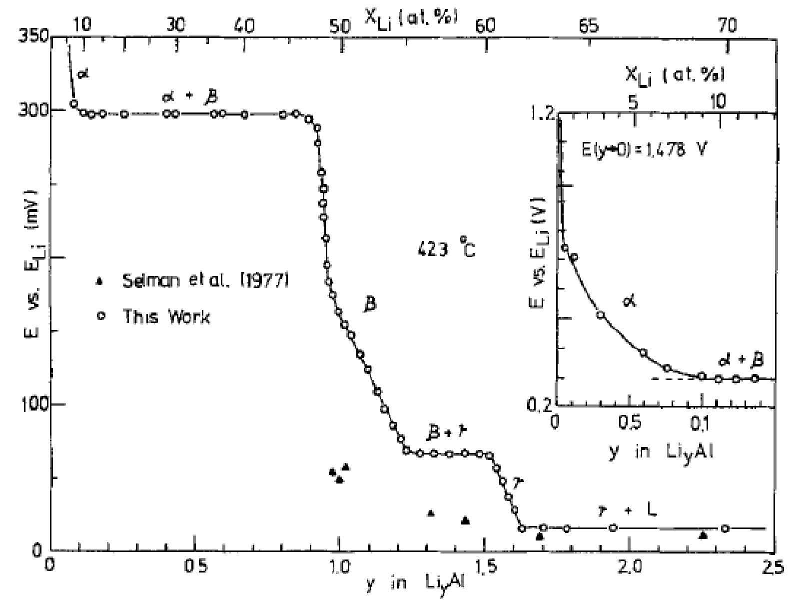
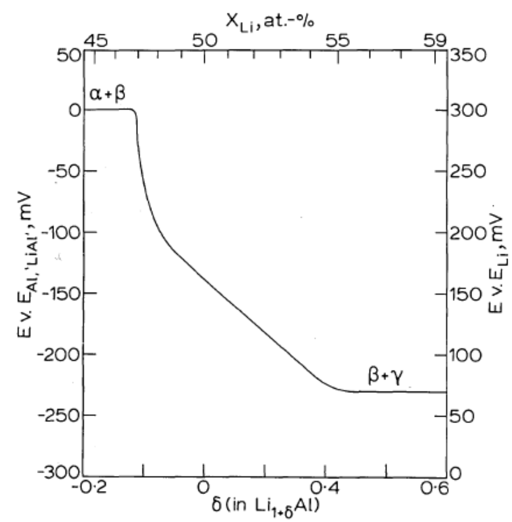


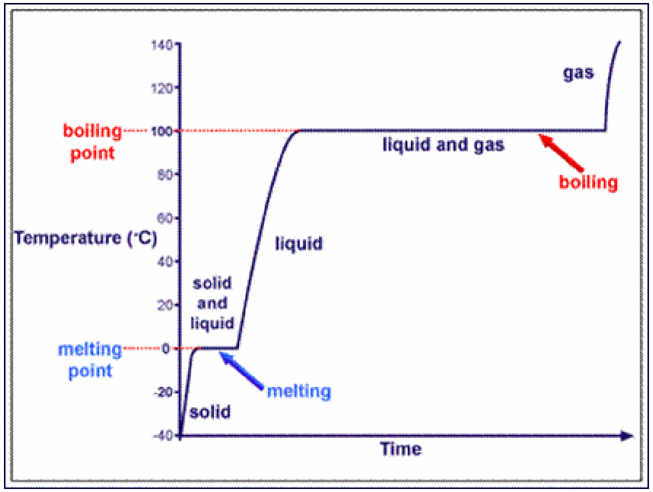
Fig. 2. Coulometric titration curve for lithium-aluminum system at 423°C.

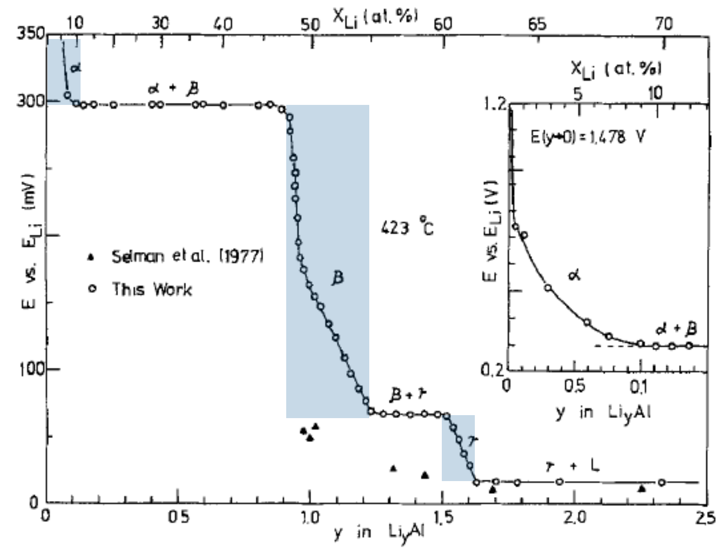


4 Coulometric-titration curve for 'LiAl' at 415°C

Analogy:

Temp vs Enthalpy Change & OCV vs degree of lithiation curve





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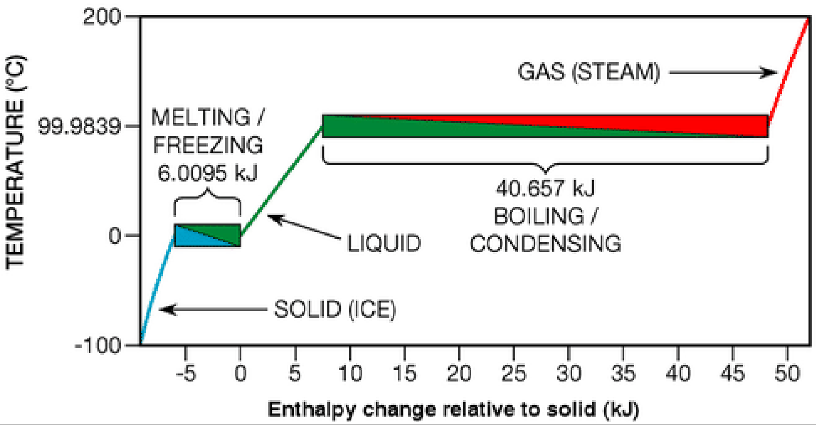
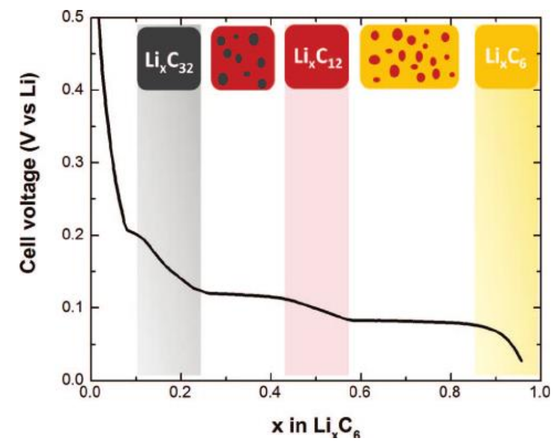
Temperature / Enthalpy Relationship of 1 mol of Water through its phase changes under constant pressure



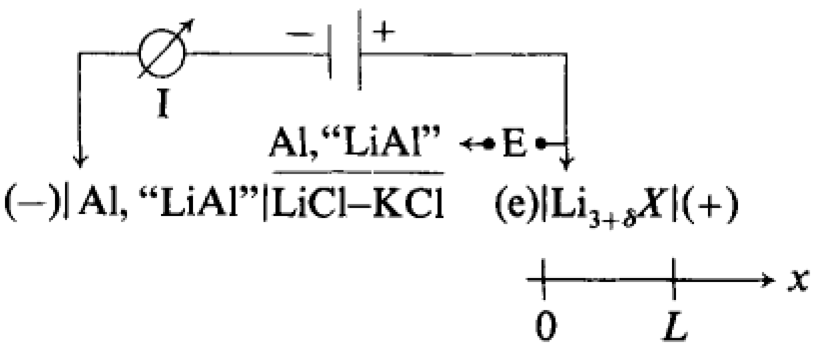


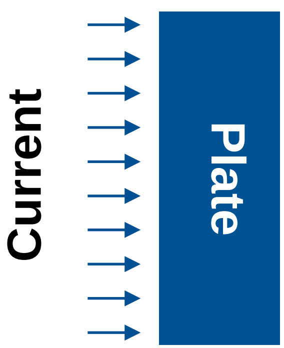
https://www.ck12.org/,
2.http://cdavisdp1011.weebly.com/phase-change-lab.html

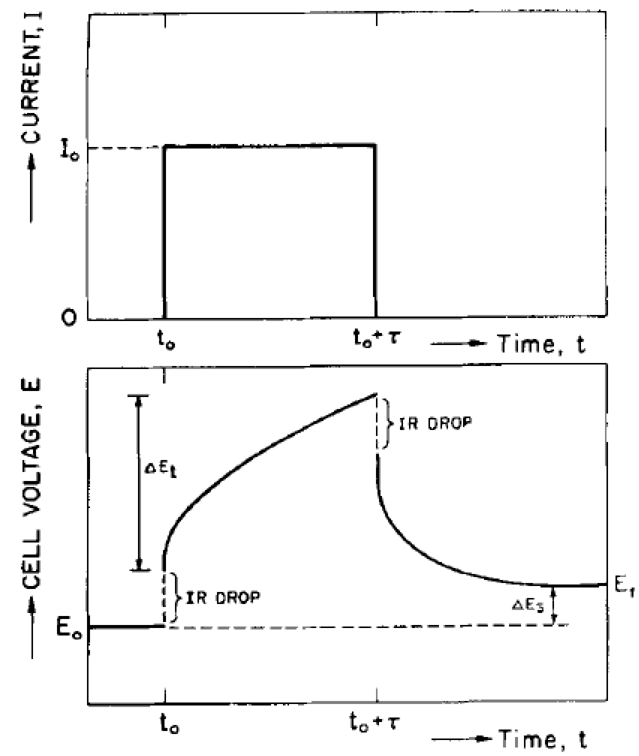
Weppner and huggins
Kevin G. Gallagher et al, JES, 2012

Experimental Setup:

Al, 'LiAl' (s) | LiCl–KCl (eutectic) | 'LiAl' (s)







Weppner and Huggins: 1981

Pictorial Description:

Mathematical Derivation

$$\frac{\partial c_i(x,t)}{\partial t} = \tilde{D}\,\frac{\partial^2 c_i(x,t)}{\partial x^2} \qquad [28]$$

with the initial and boundary conditions

$$c_i(x, t=0) = c_o \quad (0 \leqq x \leqq L) \qquad [29]$$

$$-\tilde{D}\,\frac{\partial c_i}{\partial x}\bigg|_{x=0} = \frac{I_o}{Sz_iq} \quad (t \geqq 0) \qquad [30]$$

$$\frac{\partial c_i}{\partial x}\bigg|_{x=L} = 0 \quad (t \geqq 0) \qquad [31]$$

$$c_i(x=0,t) = c_o + \frac{2I_o\sqrt{t}}{Sz_iq\sqrt{\tilde{D}}}\sum_{n=o}^{\infty}\left(\mathrm{ierfc}\left[\frac{nL}{\sqrt{\tilde{D}t}}\right] + \mathrm{ierfc}\left[\frac{(n+1)L}{\sqrt{\tilde{D}t}}\right]\right) \qquad [32]$$

with $\mathrm{ierfc}(\lambda) = [\pi^{-1/2}\exp(-\lambda^2)] - \lambda + [\lambda\,\mathrm{erf}(\lambda)]$,

$$\frac{dc_i(x=0,t)}{d\sqrt{t}} = \frac{2I_o}{Sz_iq\sqrt{\tilde{D}\pi}} \quad (t << L^2/\tilde{D}) \qquad [33]$$

$$dc_i = \frac{N_A}{V_M}\,d\delta \qquad \Delta\delta = \frac{I_o\tau M_B}{z_A m_B F}$$

$$\frac{dE}{d\sqrt{t}} = \frac{2V_M I_o}{SFz_i\sqrt{\tilde{D}\pi}}\,\frac{dE}{d\delta} \quad (t << L^2/\tilde{D})$$

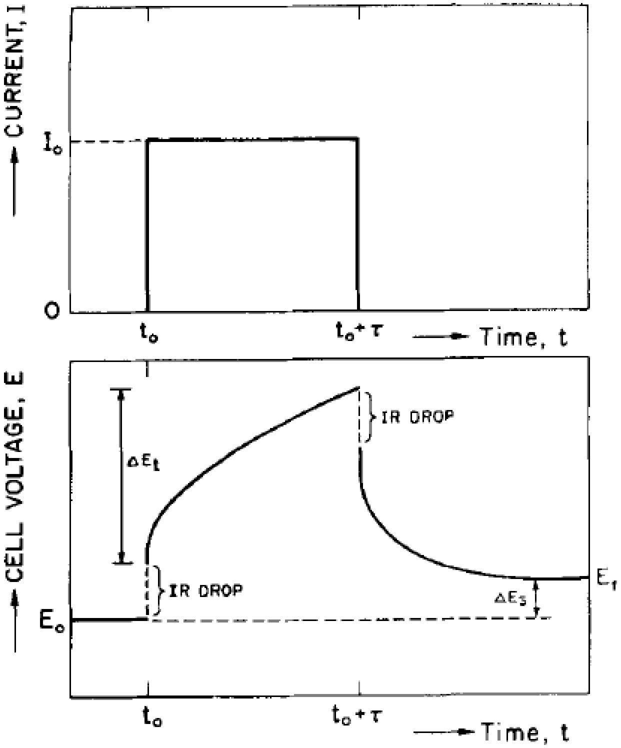
$$\tilde{D} = \frac{4}{\pi}\left(\frac{V_M}{SFz_i}\right)^2\left[I_o\left(\frac{dE}{d\delta}\right)\Big/\left(\frac{dE}{d\sqrt{t}}\right)\right]^2 \quad (t << L^2/\tilde{D})$$

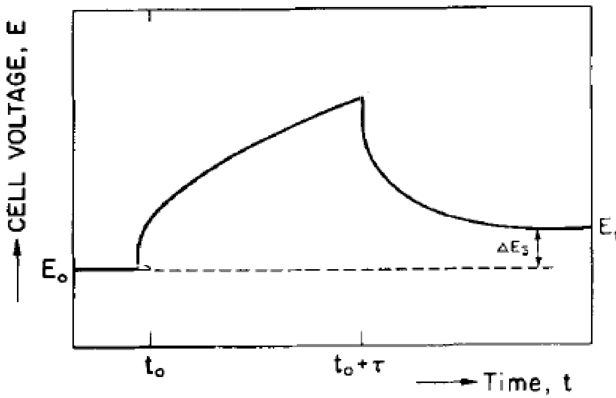
$$\tilde{D} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B S}\right)^2\left[\frac{\Delta E_s}{\tau\left(\frac{dE}{d\sqrt{t}}\right)}\right]^2 \quad (t << L^2/\tilde{D}) \qquad [37]$$

$$\tilde{D} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \quad (\tau << L^2/\tilde{D}) \qquad [38]$$

Weppner and Huggins: 1981

Processing of the Data:





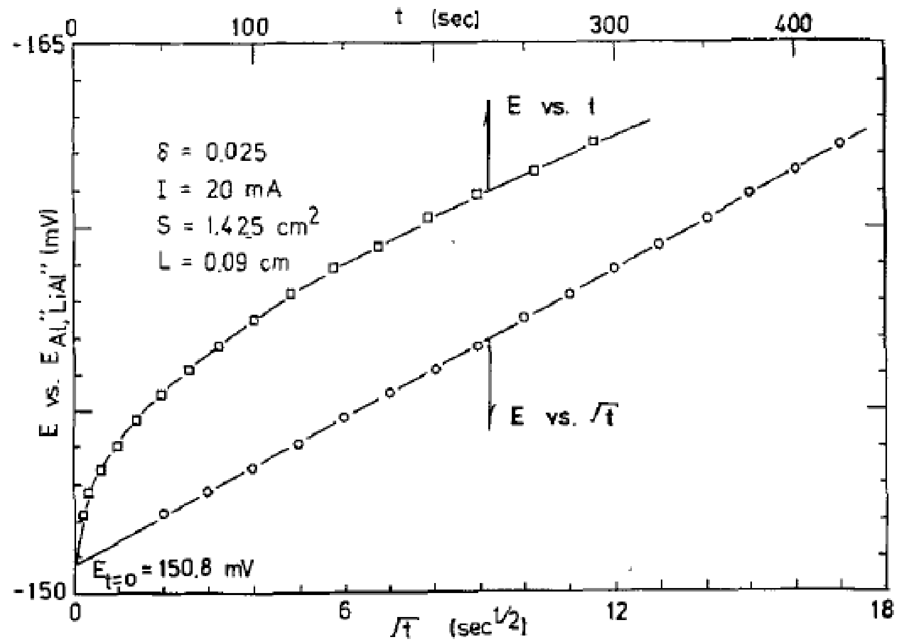
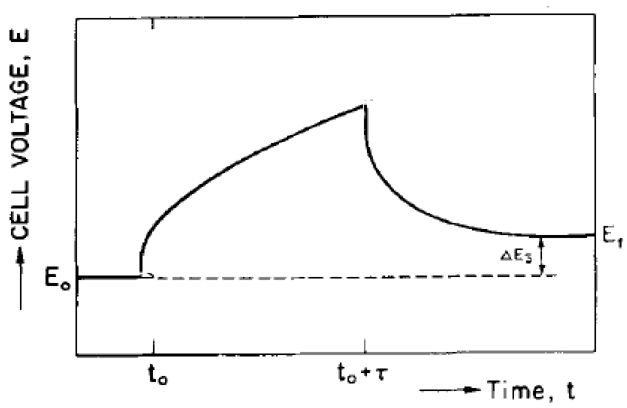


Fig. 11. Time dependence of voltage using GITT

Weppner and Huggins

Another Set of Data



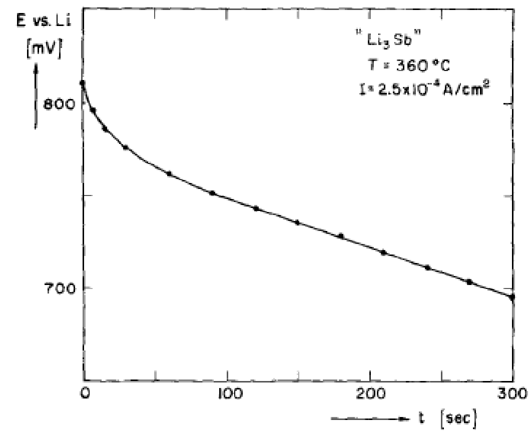


Fig. 3. Typical transient voltage change of the galvanic cell with a Li_3Sb sample after a constant current of 2.5×10^{-4} A cm^2 was applied. LiCl-KCl(e) was used as a molten salt electrolyte, and two-phase Al, LiAl mixtures used as counter and reference electrodes.

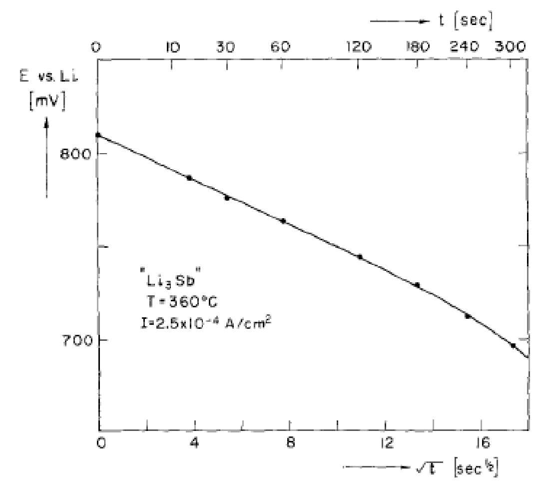


Fig. 4. Representation of the transient voltage of the galvanic cell as a function of the square root of the time. The experimental conditions were the same as those of Fig. 3.

Weppner and Huggins

Self vs Chemical Diffusivity

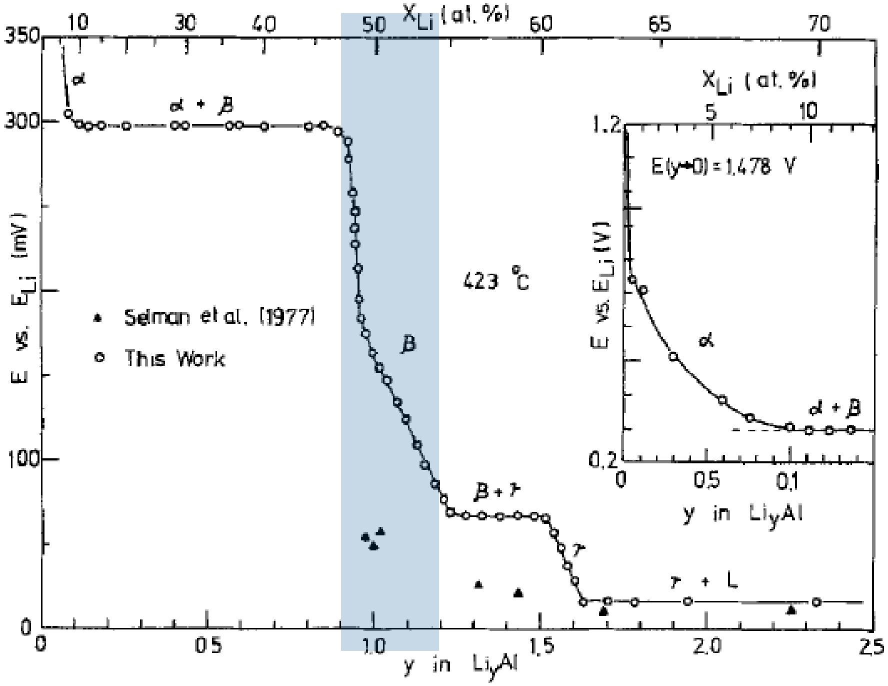


Fig. 2. Coulometric titration curve for lithium-aluminum system at 423°C.

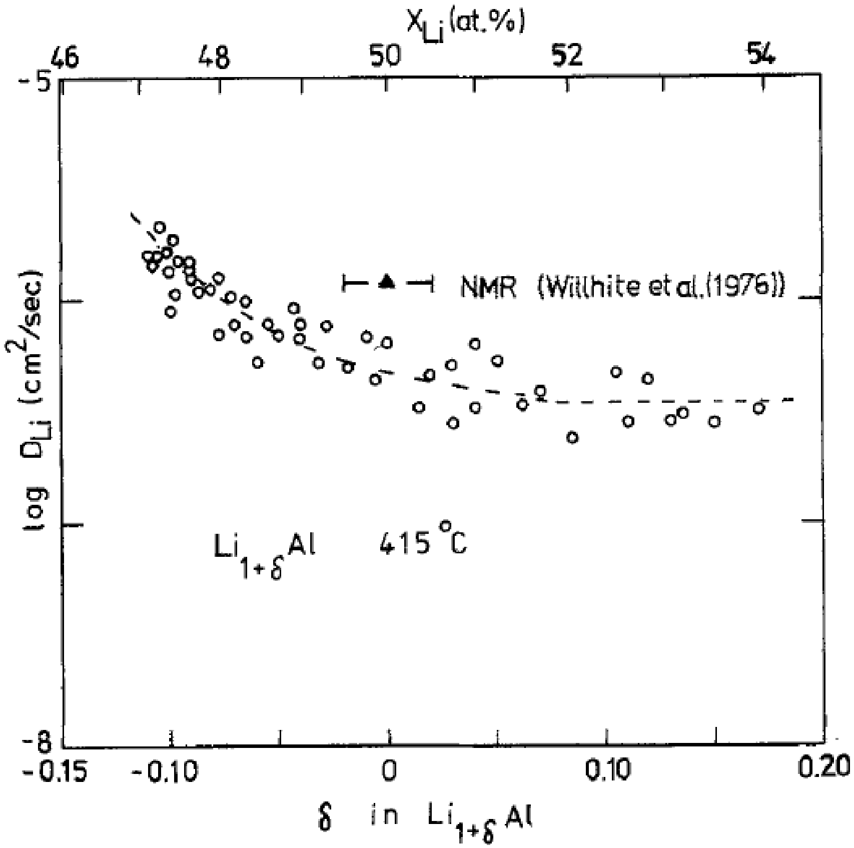
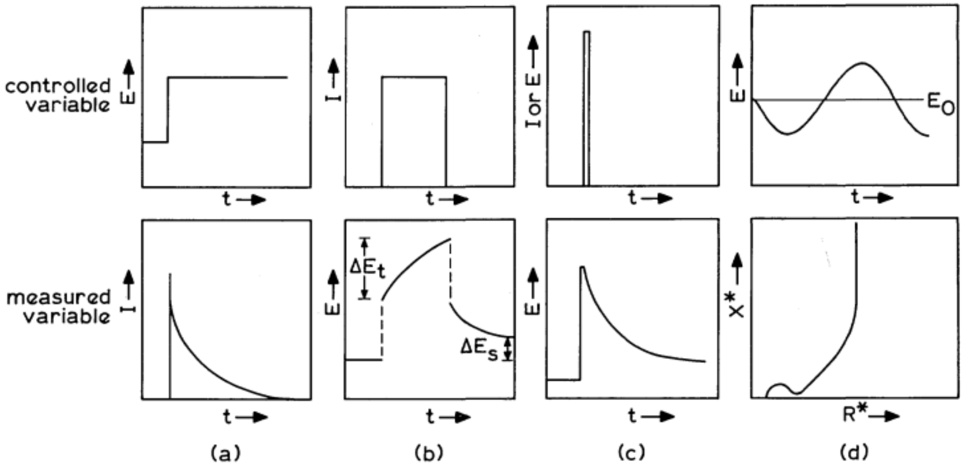
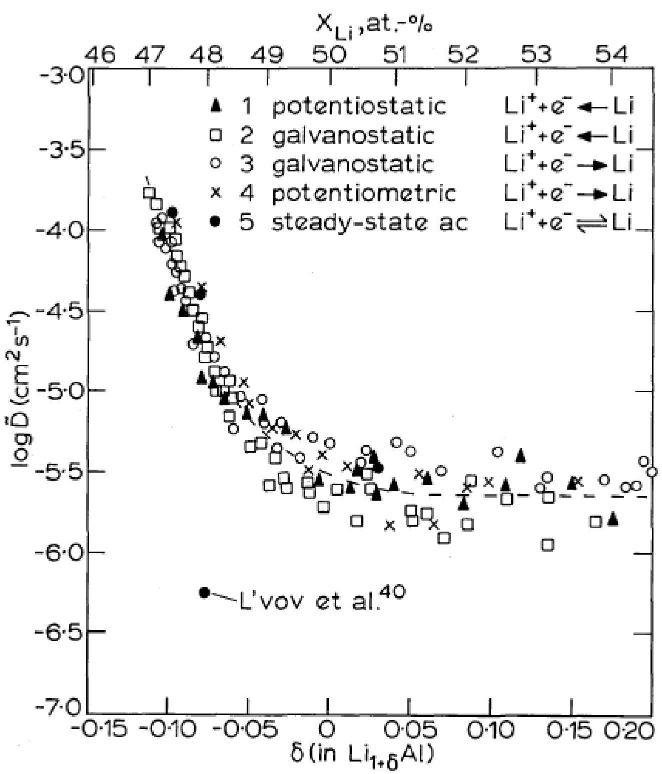


Fig. 13. Variation of diffusivity of Li in "LiAl" with composition at 415°C.

Weppner and Huggins

Summary:



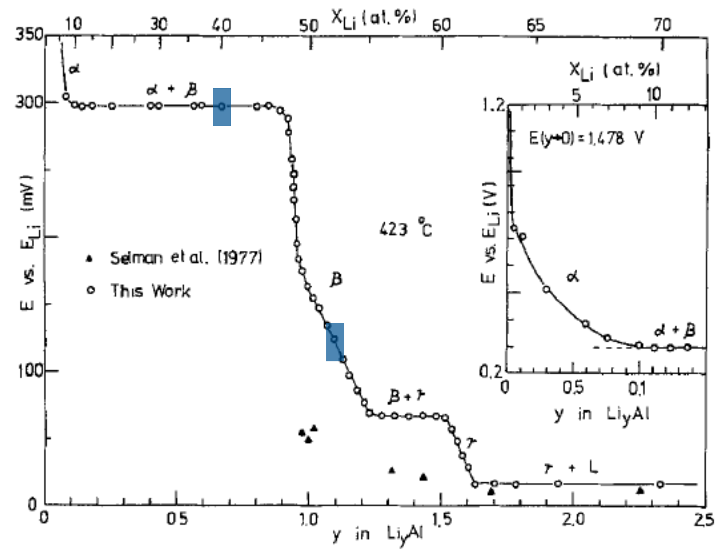


Weppner and Huggins

Consider Two Following Experiments:

at different OCV points (or initial concentration) having zero and non-zero slope.

- ❑ Consider the two following exp.
  - ❖ Slope of OCV is not zero
  - ❖ Slope of OCV curve is zero
- ❑ What will happen to the dynamic response?
- ❑ In case slope is zero, what information can we get.
- ❑ Can we use that information.



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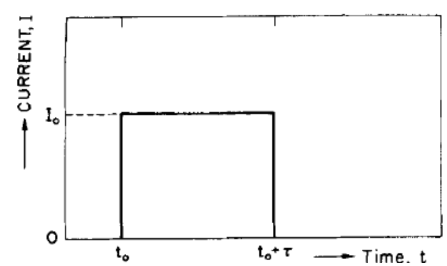
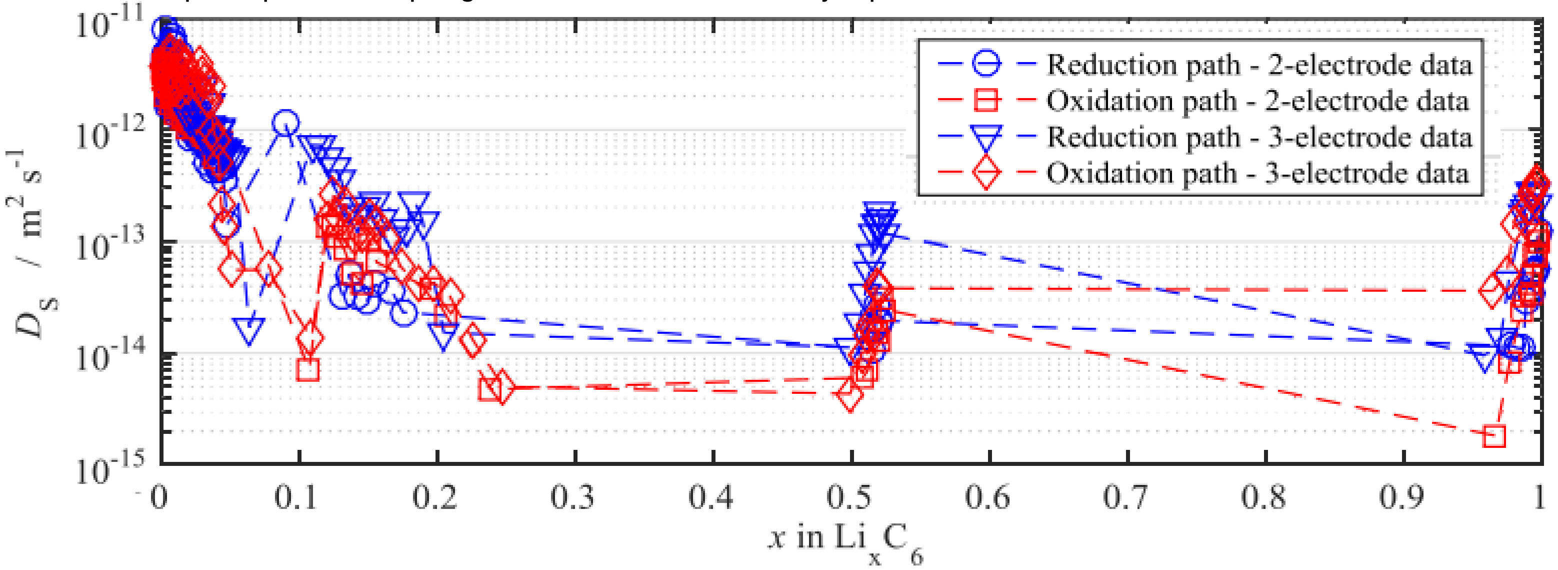
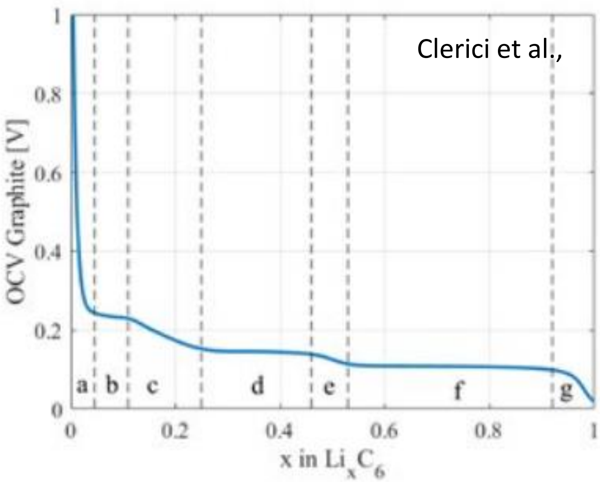


Weppner and Huggins

Li-C_6 System

Simon Malifarge et al. (Charles Delacourt)
https://iopscience.iop.org/article/10.1149/2.1591714jes/pdf





Porous Electrode vs Solid Plate

- Discussion.
- Effect of electrolyte transport

Reference:

- Weppner and Huggins: work between 1977-81

Parameters: