Examination	**EEN016 Lithium-ion battery systems for vehicles and large-scale energy storage**
	Tuesday April 7, 2020, 14:00
Lecturer:	Torbjörn Thiringer/Zeyang Geng
Help:	Everything except asking someone
Solutions:	Course Homepage a week after the exam
Mark list:	Before 4 weeks after the exam
Complaints:	Thursday, May 7, 12.15-13.00, Uno Lamms room/Zoom

The limit for a 3 on the exam is 20 p Grade 4 is 30p and grade 5 is 40p. Approved labs and project is also required. Observe that the questions are not arranged in any kind of order.

Observe that the numbering of the answer papers must be chronological. Disordered numbering will lead to 0 points on the exam.

Motive your choices, purely writing answers or putting up final expressions without derivations gives 0 points.

Check-up times: 15.15 and 16.45. Please mail questions to torbjorn.thiringer@chalmers.se and I will try to answer around these times. A personal zoom meeting is also possible, then send a link to torbjorn.thiringer@chalmers.se and zeyang.geng@chalmers.se. You can also call 0723-850969, please try to stick to the approximate times. Of course, for a high emergency, please feel free to call anytime.

Question 1 (13p)

Download the file "EEN016_exam_20200407_example.mph" from Canvas and open it in COMSOL Multiphysics 5.4.

Some of the parameters used in the model are listed below

Parameters	Negative electrode	Separator (electrolyte)	Positive electrode
Length (μm)	46	18	44
Particle Radius (μm)	10		5
Porosity	0.29	0.4	0.21
Volume fraction of the solid	0.49	-	0.57
Electronic conductivity (S/m)	100		0.1
Diffusion coefficient in the solid phase (m^2/s)	6.8e-15		5e-13
Diffusion coefficient in the liquid phase (m^2/s)		1e-10	
Electrolyte conductivity (S/m)		0.01	
Initial concentration (mol/m^3)	2285.2	1000	44100

a) The positive electrode used in this simulation is NMC111 and in the latest research NMC811 is an alternative. What is the change raw material usage in the electrode NMC811 compared with NMC111. (1p)

The amount of Ni is increased, and the amount of Mn and Co are decreased.

b) What could reasons be for using this new type of electrode material (2p)

Cost and environment impact.

c) What are the capacities of the electrodes? (2p)

The maximum concentration of LTO is 22852 mol/m^3 and it is 49000 mol/m^3 for NMC111. The area of the electrode is 1 m^2. (Those values can be found in the given COMSOL file).

The capacity of LTO electrode is

$$1\ m^2\ \times 46\ \mu m\ \times 0.49 \times 22852 \frac{mol}{m^3} \times 96485 \frac{F}{mol} = \ 13.8Ah$$

The capacity of NMC electrode is

$$1\ m^2\ \times 44\ \mu m\ \times 0.57 \times 49000 \frac{mol}{m^3} \times 96485 \frac{F}{mol} = \ 32.9Ah$$

Birth month	Task
January February March April	Change the initial lithium ion concentration to be 90% in the negative electrode and (birth date) % in the positive electrode. If you were born in 15th January, the initial concentration in the positive electrode is 15%. Perform a discharge simulation with 10 A/m^2 discharge current and 2 V cut off voltage. What is the discharge capacity (in Ah) in this scenario? Change the electrode area to be 5 cm^2. What is the discharge capacity (in Ah)?
May June July August	Perform a current step simulation with 20 A/m^2 charge current. What is the 10 seconds resistance (in Ohm)? Change the positive electrode conductivity to be (birth date) S/m and run the simulation again. If you were born in 15th March, the electrode conductivity is 15 S/m. What is the 10 seconds resistance (in Ohm)? In reality, how can the electrode conductivity be improved?
September October November December	Add double layer capacitance in both electrodes. The capacitance in the positive electrode is 0.2 F/m^2 and in the negative electrode is (birth date) F/m^2. If you were born in 15th May, the double layer capacitance in the negative electrode is 15 F/m^2. Perform a potentiostatic EIS from 1 kHz to 1 mHz. Chose the perturbation voltage and motivate your choice.

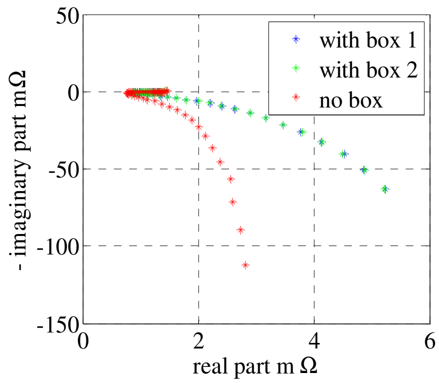
Question 2 (4p)

An EIS test has been conducted from 10 to 100000Hz. The result for the low frequency, shows a good agreement. However, measurements conducted with the cell placed in a metal box show different results for the higher frequency range.

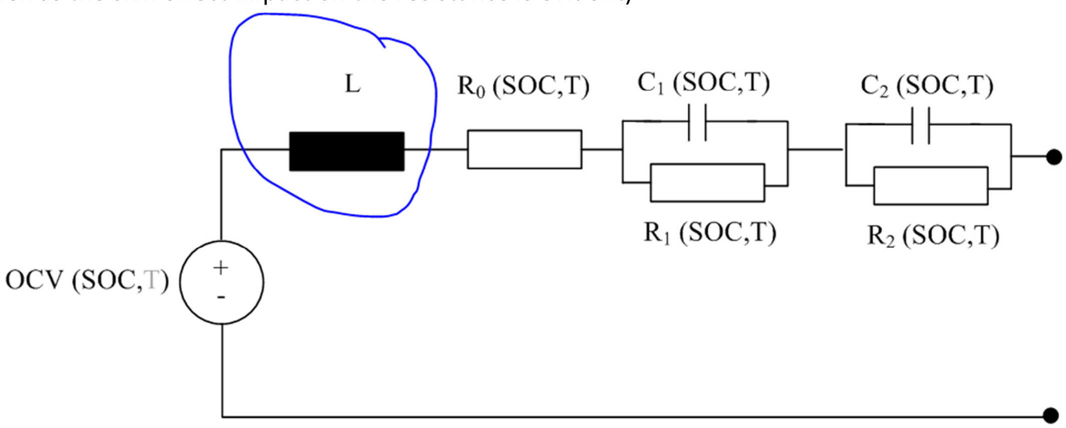
a) Why? (2p)

Parasitic inductance and capacitance. As well as skin effect.

b) Draw an equivalent circuit of the battery cell explaining what equivalent circuit parameters in the box that are affected, by the placement of the cell in the metal box. (2p)

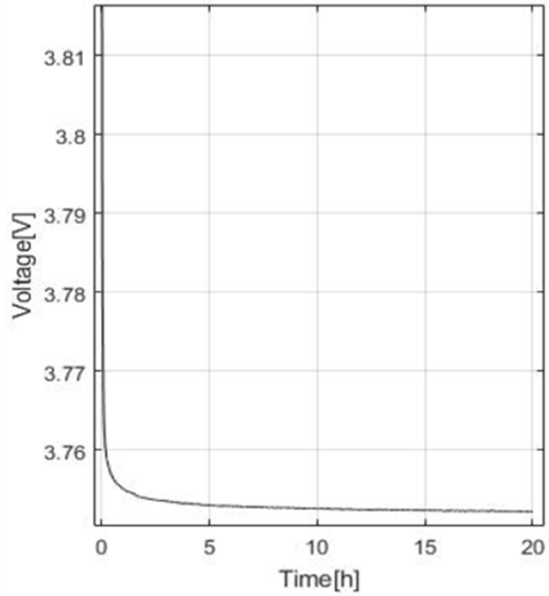


At this high frequency is the inductance that governs the behaviour. (Also parasitic capacitance as well as the skin effect impact on the resistance is evident)



Question 3 (4p)

A relaxation of a cell, following the interruption of a 30 A 10 minute charging pulse is presented in the figure



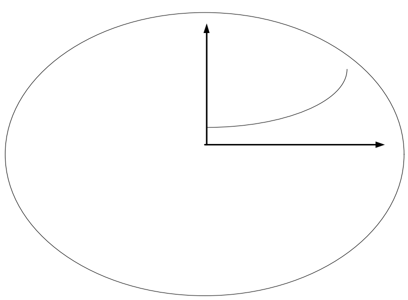
What physical properties is it in the cell that forms the shape of the voltage during the relaxation?

It is the diffusion in the electrode particles that ceases to exist. (The uneven distribution of particles slowly goes towards an even distribution, which takes a very long time)

Question 4 (2p)

a) Sketch the concentration distribution in a graphite particle during charging. What is the governing process that causes the concentration gradient? (2p)

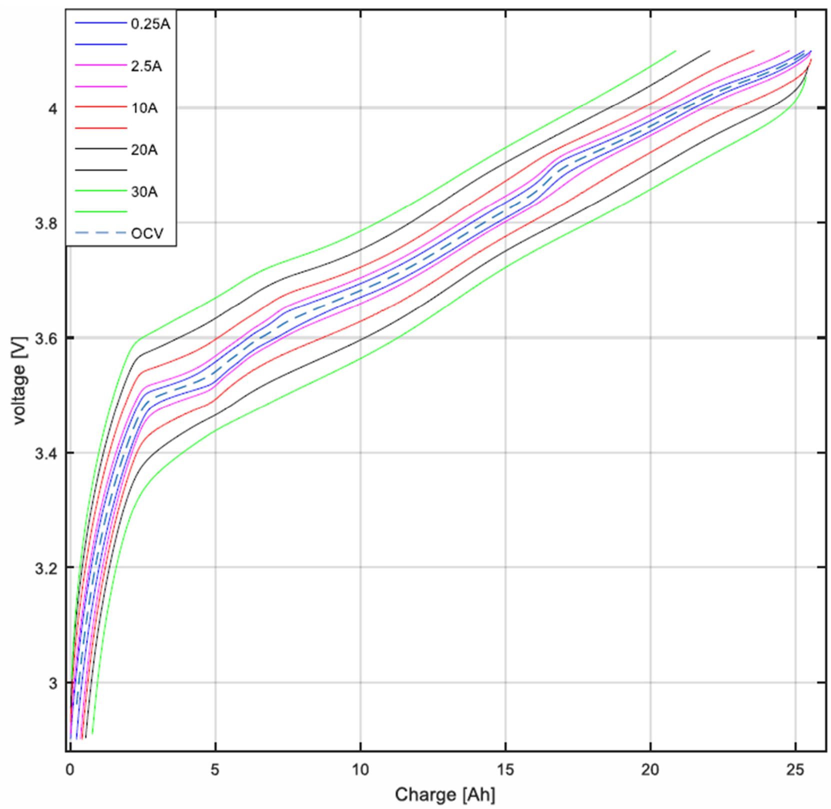
During charging Li-Ion particles are being put into the anode (graphite) particles. So in the middle the concentration is lower compared to the outer part of the particle



It is of course the current density, but also the diffusion time constant.

Question 5 (10p)

Lithium Ion batteries typically have a hysteresis, that can be noted in measurements. Below is the charging and discharging of a 26 Ah cell presented.



a) What does it mean with a hysteresis? Estimate its value (2p)

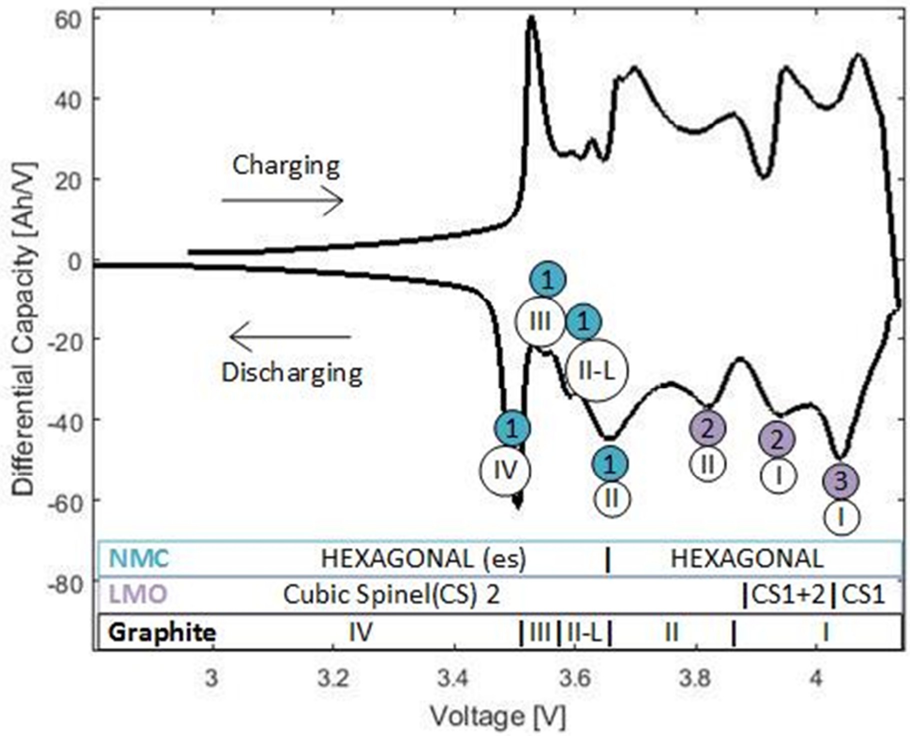
Hysteresis means that the relaxed voltage depends on from which way the SOC-level was reached. It is higher after a charging event and lower after a discharge event. The 30 A charge and discharge-curve, the hyestersis plays a minor role compared to the voltage drop due to the resistance. The charge-discharge gives a voltage difference value of 0.22 V 0.22/(2*30)=3.7 mOhm. For a 0.25 A charge and discharge this means a Resisitve part of the voltage drop of DV=2*0.25*3.7=1.85 mV. The voltage difference measured in the figure is about 25 mV, so approximately the hysteress voltage is U_hyst=(25-1.85)/2= 12 mV.

b) There are some 'bumps', especially when looking at the blue line, why is that? (3p)

They indicate phase shifts. In principle, the Li-Ion particles has filled (or depleted) from going into one type of positioning in the anode and cathode particles structrues, and starts to fill the next level

c) Draw a sketch of the incremental capacity analysis result from the 0.25 A and the 30 A charge and discharge (5p)

For 0.25 A the peaks are sharper, and positioned almost at the same voltage. For the 30 A charge they are much wider and the charge peaks occur at a higher voltage then the discharge peaks due to the impact of internal resistance



Question 6 (7p)

An experimental cell has a capacity of 107 Wh/kg, the dimensions can be found below.

See if you can redo the cell and optimise the energy density. Motivate your choices, violation of 'unchangable' properties should of course not be done. Try to keep the cell thickness approximately the same. If something is missing in the parameter list, feel free to make a reasonable addition/assumption.

What value did you manage to reach ? What measures did you take to get there ? (7p)

Thickness of Copper	30 µm (double coated)
Thickness of positive Aluminium	20 µm (double coated)
Thickness of separator	15 µm
Thickness of cathode	50 µm
Thickness of anode	40 µm
Loading Density of LFP (including binders and additives)	1.6 g/cm3
Loading Density of Graphite (including binders and additives)	1.7 g/cm3
Weight percentage of LFP in cathode	94%
Weight percentage of Graphite in anode	90%
Theoretical Capacity of LFP	160 mAh/g
Theoretical Capacity of Graphite	350 mAh/g
Density of Copper	8.96 g/cm3
Density of Aluminium	2.7 g/cm3
Density of Electrolyte	1.35 g/cm3
Volume excess of electrolyte	3 time
Separator data	3 g/m2 90% porosity
Weight of casing	10 g
Area of electrode	0.65 m2
Nominal voltage of the cell	3.4V

First a check:

```
PE_weight = PE_thickness*area*1.6/1e-6  = 52 g
PE_cap = PE_weight*0.16*0.94 =7.82 Ah
NE_weight = NE_thickness*area*1.7/1e-6 = 44.2 g
NE_cap = NE_weight*0.35*0.9 = 13.92 Ah

NP_ratio = NE_cap/PE_cap= 1.7803



sep_weight = area*3=1.95 g
al_weight = 20e-6*area*2.7/1e-6/2 =17.55 g
cu_weight = 30e-6*area*8.96/1e-6/2 =87.36 g

electrolyte_volume_excess = 3*15e-6*area*0.9 =26.3 mm^3
electrolyte_weight = electrolyte_volume_excess*1.35/1e-6  =35.5 g

total_weight=PE_weight+NE_weight+sep_weight+al_weight+cu_weight+electrolyte
_weight+10   =   248.5988 g

EnergyCapacity=PE_cap*3.4 =26.6 Wh

energy_density = PE_cap*3.4/(total_weight*1e-3)=107 Wh /kg
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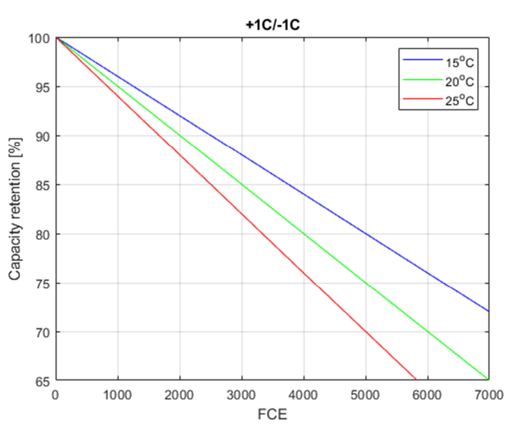
OK !

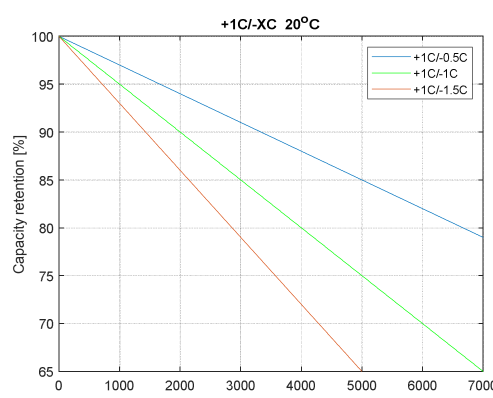
So, the N/P ratio is a bit high, 1.2 is a common value, let us try to increase the capacity of the positive electrode and make the negative smaller.

Moving 8.5 um from the NE to the positive electrode gives 125 Wh and 1.2 in N/P ratio
Moving 12 um from the NE to the positive electrode gives 133 Wh, and 1 in N/P ratio have LiPlating

Question 7 (10p)

A vehicle Li-ion battery is tested for ageing and the cells have the following ageing trends. The full battery has a usable capacity of 20 kWh, consume 0.2 kWh/km and is driven 100 km every day with various speeds. The car is always charged with 1C current. The engineer at a car manufacturer has been assigned to make an empirical ageing model based on this received test data.

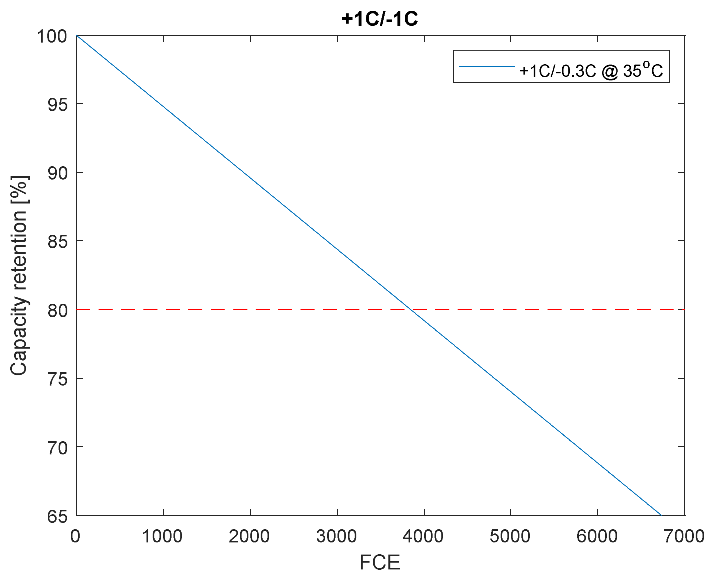




a) Help the engineer to create an empirical ageing model based on this available data regarding temperature and C-rate. Appropriate approximations regarding the empirical model are quite sufficient. Be clear with what assumptions you make. (4p)

Ans: Q=100-FCE.*(0.004+(T-15).*0.0002);

b) Use the derived empirical ageing model to estimate the driving length until 80% capacity retention for a driver using an average discharge current of 0.3C and an ambient temperature of 35°C, has been reached, state the assumptions you make. (2p)



3800 cycles corresponding to 380 000 km

c) The engineer is not 100 % pleased with the estimation, can you find a reason for the dissatisfaction (not the fact that the calendar ageing has been ignored). (2p)

He is extrapolating outside the region where the empirical model can be assumed to be valid

.

d) The engineer now obtains new information that the cells after 6 years have lost 10 % of their capacity, regardless of storage temperature. What is the estimated degradation once the calendar ageing has been included? (2p)

3800 cycles corresponds to 10.4 years. 10.4 years give 10.4/6*10%=17.3 % degradation . In total 62.7 % of the initial capacity is still available in the battery.

Formula sheet for the exam

Step response of a RC circuit

$$u(t) = iR\left(1 - e^{-\frac{t}{RC}}\right) + u(0)$$

RMS (root-mean-square) current

$$I_{RMS} = \sqrt{\frac{1}{T}\int_0^T i^2 dt}$$

The effective conductivity in a porous material

$$\sigma_{eff} = \sigma\frac{\Phi}{\tau} = \sigma\Phi^{\beta}$$

The effective diffusion coefficient in a porous material

$$D_{eff} = D\frac{\Phi}{\tau^2}$$

Active material specific capacity

$$Q = \frac{nF}{M_w}$$

Butler-Volmer relation

$i = i_0\left(exp\left(\frac{\alpha_a nF}{RT}\eta\right) - exp\left(-\frac{\alpha_c nF}{RT}\eta\right)\right)$ can for low currents be written as $i = i_0\left(\frac{nF}{RT}\eta\right)$

Constants:
Faradays constant 96485 Coulumb/mol
Avogadros number $6.02e^{23}$/mol
Bolzmans constant $1.38e^{-23}$ J/K
Gas constant: 8.31 J/mol/K

Volume of a sphere=$4/3\pi r^3$
Area of a sphere=$4\pi r^2$