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Real Time Monitoring and Characterizing of Li-ion Batteries Aging

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presented by

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15th of November 2013

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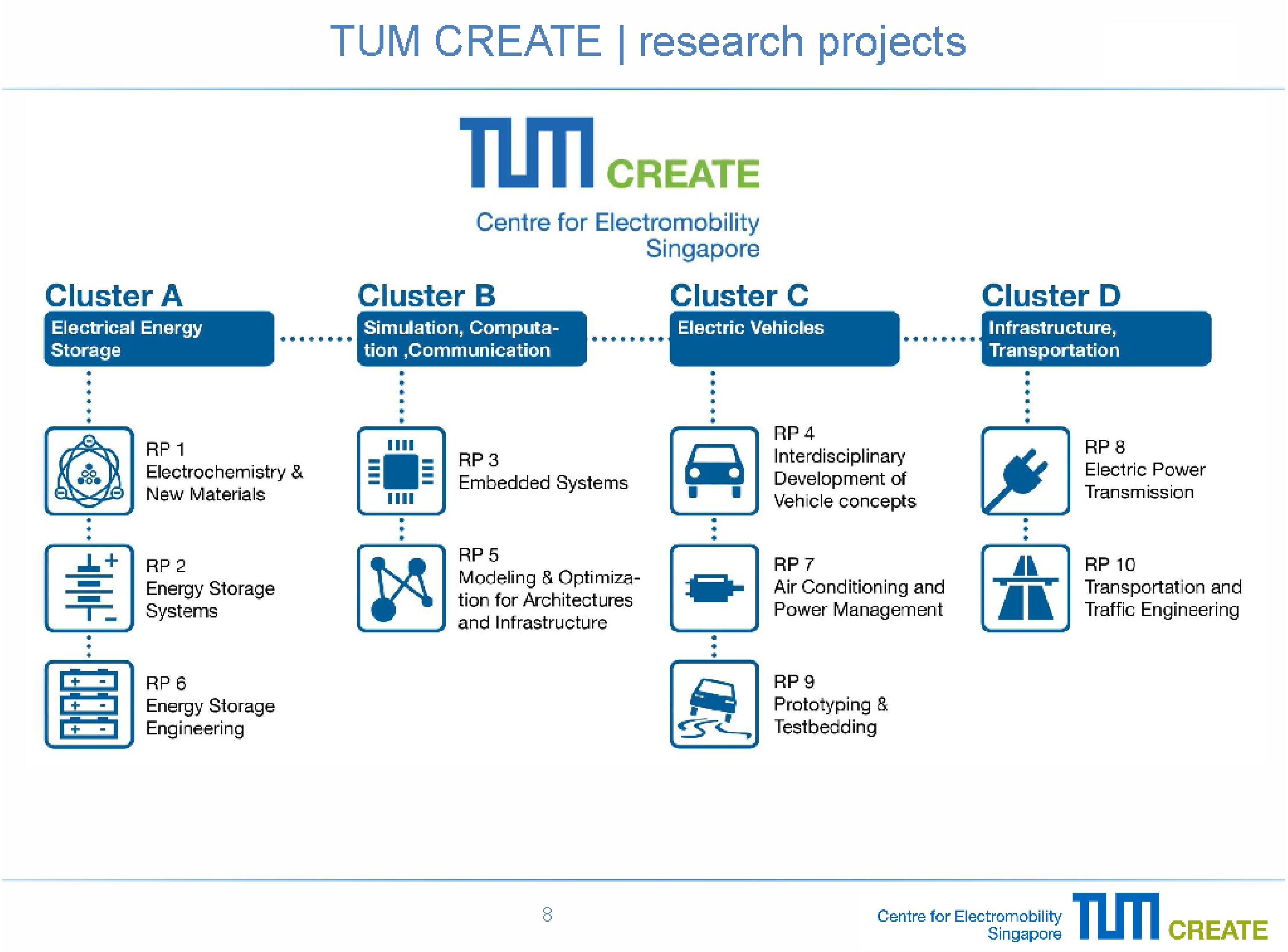
Overview of EV Program in Singapore



TUM CREATE | research projects

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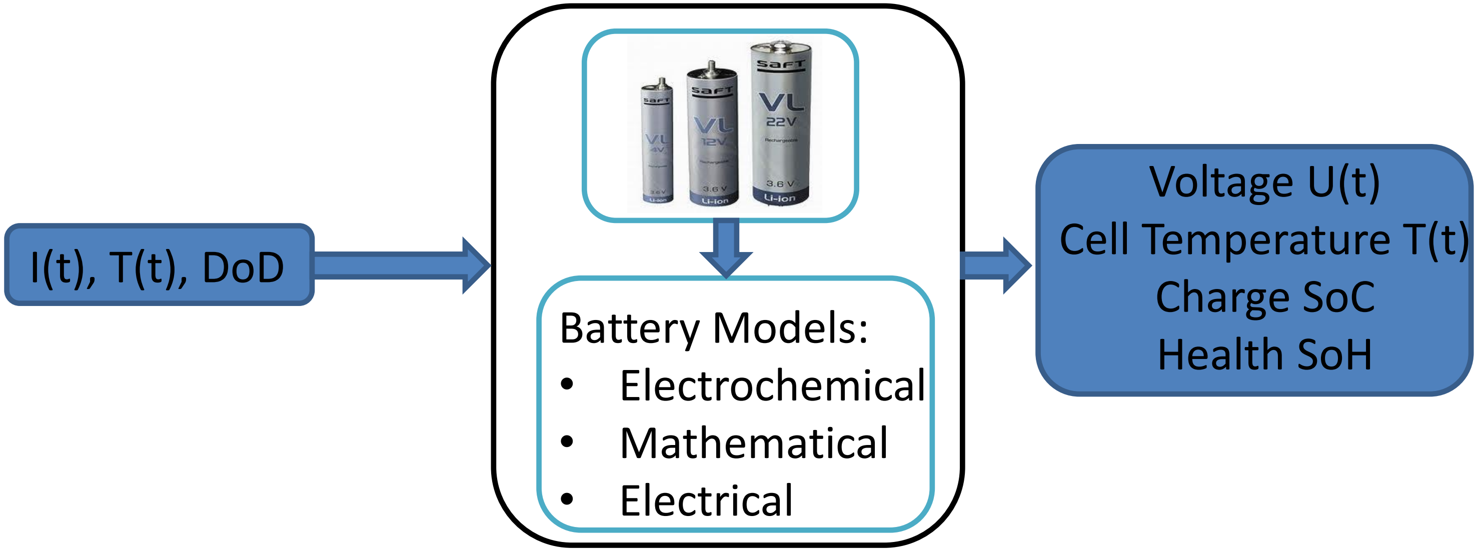
Battery modeling: Model type, Choice



I(t), T(t), DoD

Battery Models:

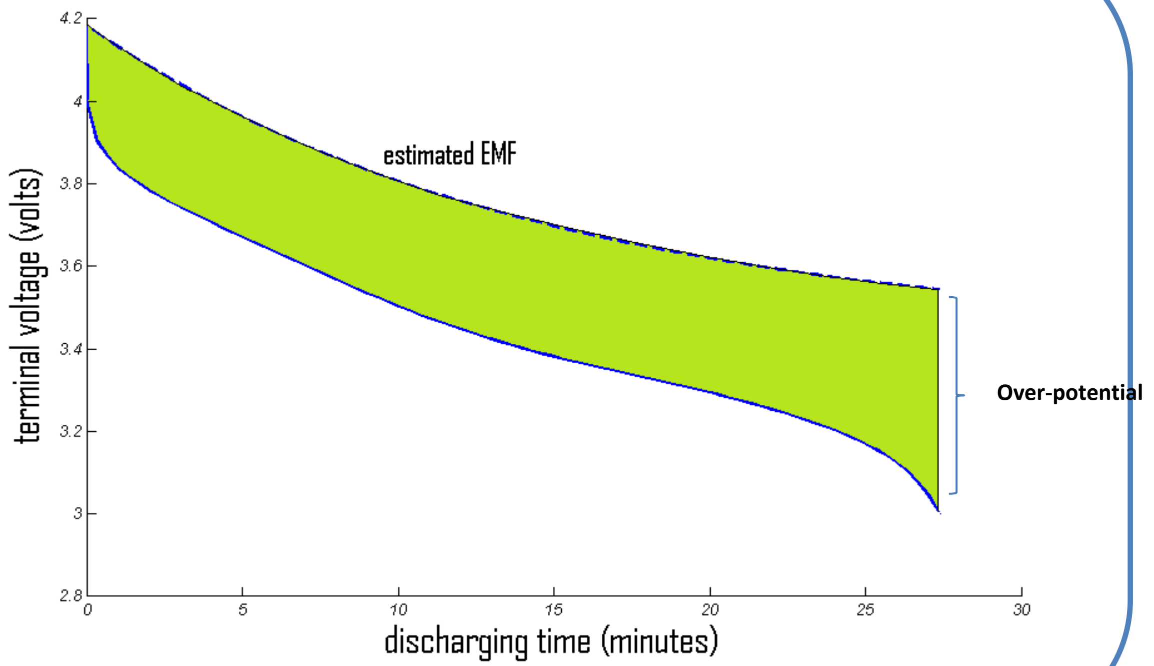
- Electrochemical
- Mathematical
- Electrical

Voltage U(t)
Cell Temperature T(t)
Charge SoC
Health SoH

- Electrochemical models ---Computationally time consuming
- Mathematical models---No direct relation between the model parameters and the electrical characteristics of the batteries.
- **Electrical model**---Electrical equivalent circuit and on-line estimation of battery states.

Source: Kroeze,R.C and Krein, P.T, "Electrical Battery Model for Use in Dynamic Electric Vehicle Simulations" IEEE. PESC,Rhodes,GRE, 2008, pp. 1336-1342

Decomposition of battery discharging curve



$$V_{terminal} = V_{emf} - \eta$$

Source: V. Pop, H.J. Bergveld, D. Danilov, P.P.L. Regtien, and P.H.L. Notten, *Battery management system: accurate state-of-charge indication for battery powered applications,* vol.9: Springer Verlag, 2008.

Development of EMF

$$V_{emf} = E^+_{eq} - E^-_{eq} \quad (1)$$

$$E^+_{eq} = E^+_0 - \frac{RT}{F}\left[ln\left(\frac{x_{Li}}{1-x_{Li}}\right) + U^+_j x_{Li} - \zeta^+_j\right] \quad (2)$$

$$E^-_{eq} = E^-_0 - \frac{RT}{F}\left[ln\left(\frac{z_{Li}}{1-z_{Li}}\right) + U^-_j z_{Li} - \zeta^-_j\right] \quad (3)$$

$$Q^+_{max} = m_1 Q_m \,, \boldsymbol{m_1 \leq 1} \quad (4)$$

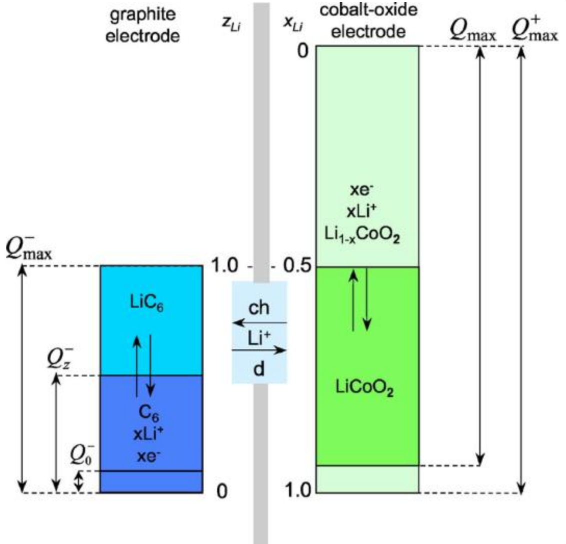
$$Q^-_{max} = m_2 Q_m \,, \boldsymbol{m_2 \leq \frac{1}{2}} \quad (5)$$

Employ the EMF expression derived by Pop et al

If SoC >50% ➔ $Q^-_0 \ll Q_{max}$, ➔ Q^-_0 *can be ignored*

$$V_{emf} = E^+_{eq} - E^-_{eq}$$

$$= E_0 - \frac{RT}{F}\left\{ln\frac{[2-(2-m_1)SoC][2m_2-(2-m_1)SoC]}{[2m_1-2+(2-m_1)SoC][(2-m_1)SoC]} + \left[\frac{U^+}{m_1} - \frac{2-m_1}{2m_1m_2}\times SoC \times (m_2U^+ - m_1U^-)\right] + \varepsilon\right\}$$

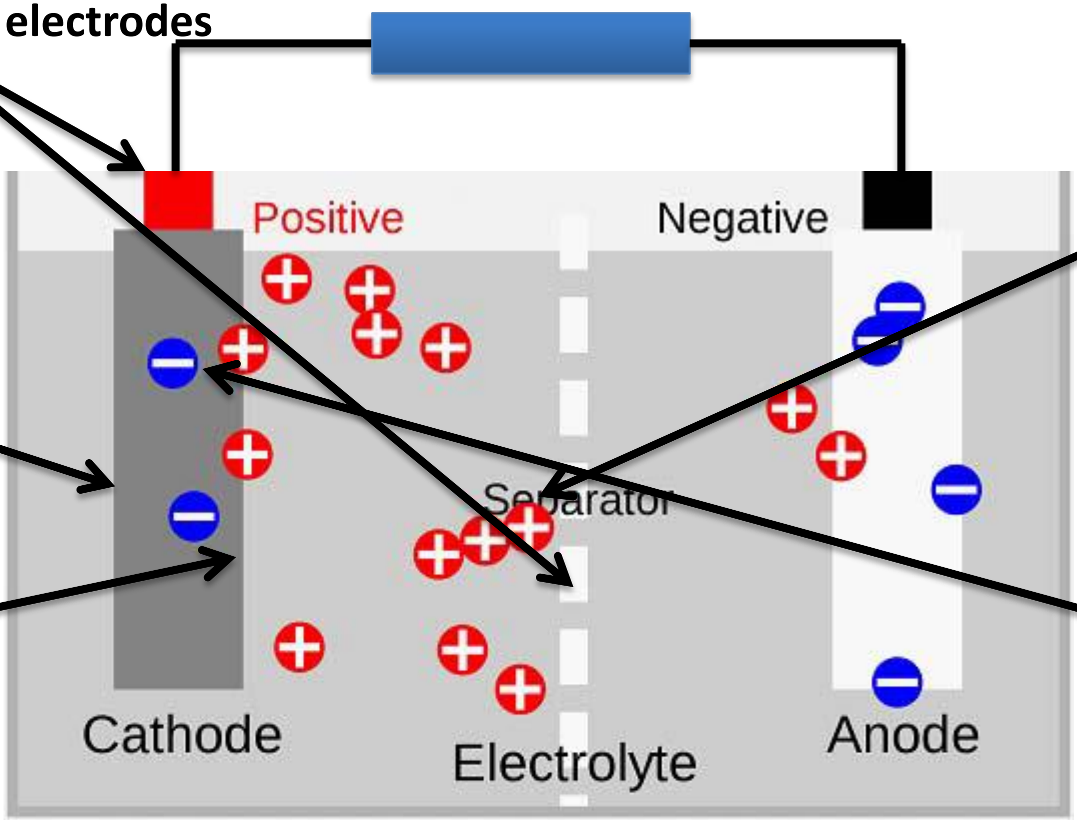


Source: V. Pop, H. J. Bergveld, P.P.L. Regien, J.H.G. Op het Veld, D. Danilov, and P.H.L. Notten, “Battery Aging and Its Influence on the Electromotive Force”, J.Electrochem. Soc, Vol.154, No.8, pp.A744-A750, 2007

Development of Over-potential

η

Electrical model of a battery : based on the principle of physical chemistry



Ohmic resistance of electrolyte and the electrodes

Butler-Volmer

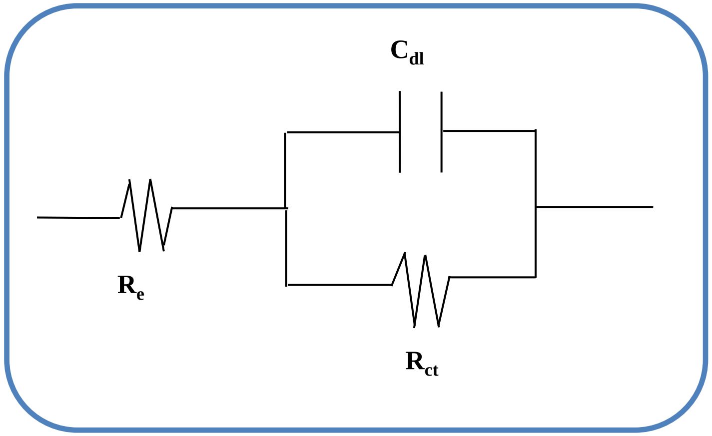
Charge transfer resistance

Mass transport (Diffusion) Warburg element

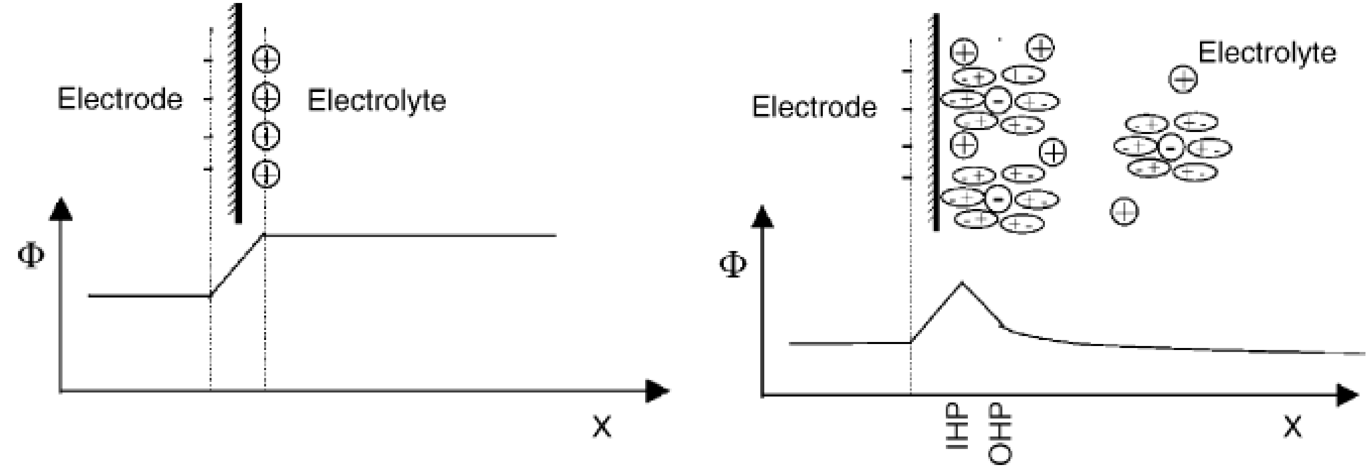
Double layer capacitance

Source: Serge.pelissier,"Battery for electric and hybrid vehicles state of the art," *IEEE. VPPC*, Lille, FR, 2010, Tutorial 2-2 part.2

Development of Over-potential : Randles' model

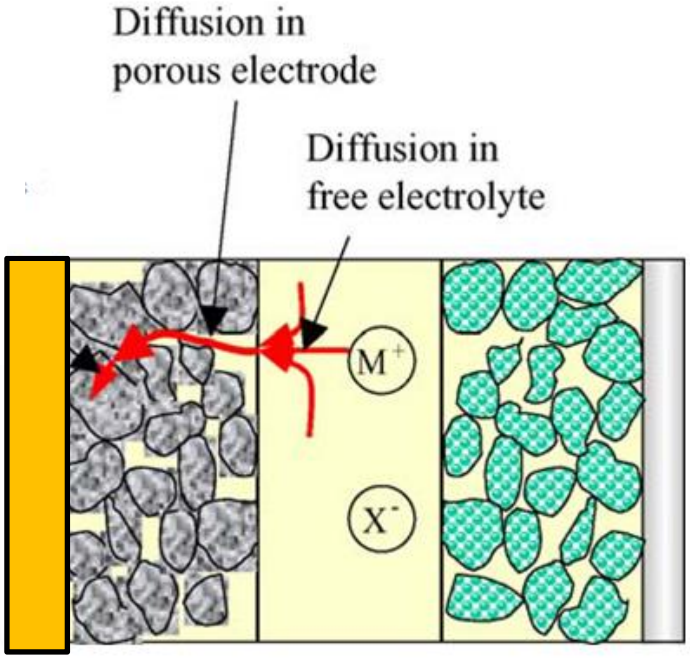


- Re: Ohmic resistance of the electrolyte and the electrodes
- Rct: active charge transfer resistance
- C_{DL}: double-layer capacitance



Source: Andreas Jossen, "Fundamentals of battery dynamics" J.Power Sources, vol.154 ,pp.530–538, 2006

Development of Over-potential : Diffusion phenomena

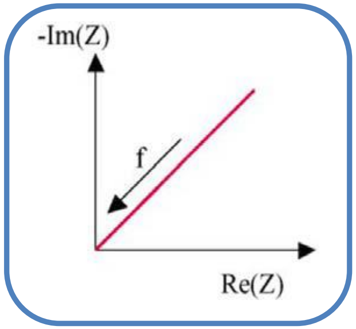


Fick's first law describes the diffusion:

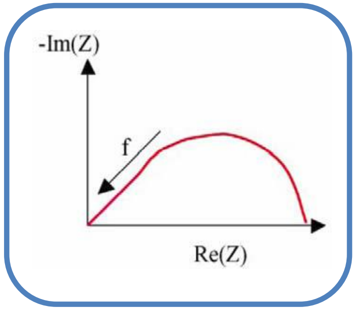
$$N_i = -D_i \frac{\mathrm{d}c_i}{\mathrm{d}z}$$

Source: Andreas Jossen, "Fundamentals of battery dynamics" J.Power Sources, vol.154 ,pp.530–538, 2006

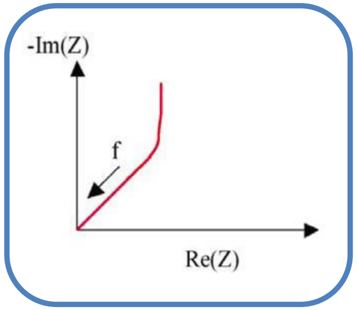
Development of Over-potential :Diffusion phenomena



Semi-infinite diffusion (Warburg impedance) :
Infinite electrode in an infinite electrolyte reservoir
No stationary state ; the impedance has a constant phase of -45° at any frequencies



Bounded diffusion :
Limited diffusion layer with ideal reservoir at the boundary
Stationary state : the electric equivalent circuit is a resistor; flux of diffused component is constant

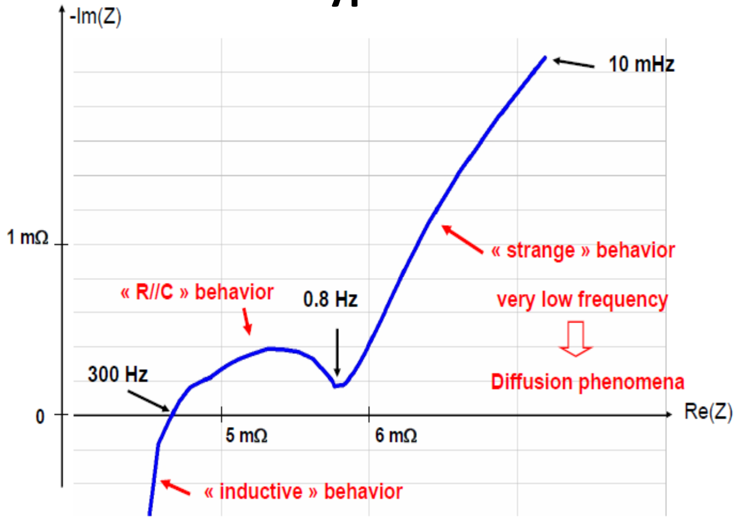


Restricted diffusion :
Limited diffusion layer with a fixed amount of electro-active substance
Stationary state : the electric equivalent circuit is a capacitor and a resistor in series; flux of diffused component is zero

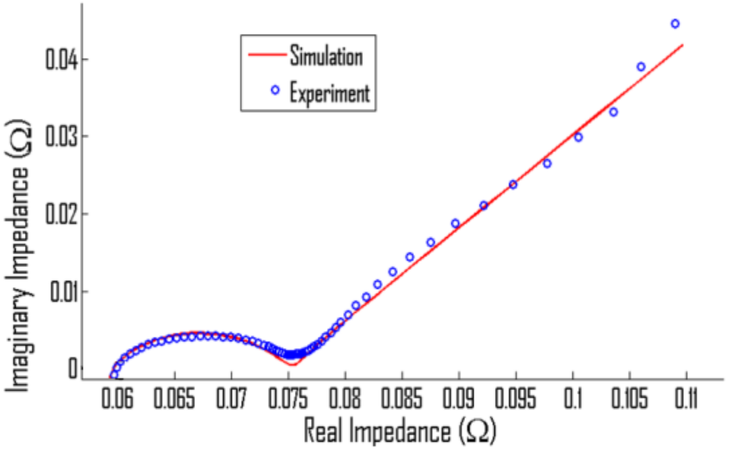
Source: Andreas Jossen, “Fundamentals of battery dynamics” J.Power Sources, vol.154 ,pp.530–538, 2006

Development of Over-potential :Warburg element

Typical



Experimental



From our EIS spectrum results, we can see that our battery diffusion belongs to the case of semi-infinite diffusion layer, which is Warburg element, and it corresponding impedance is given:

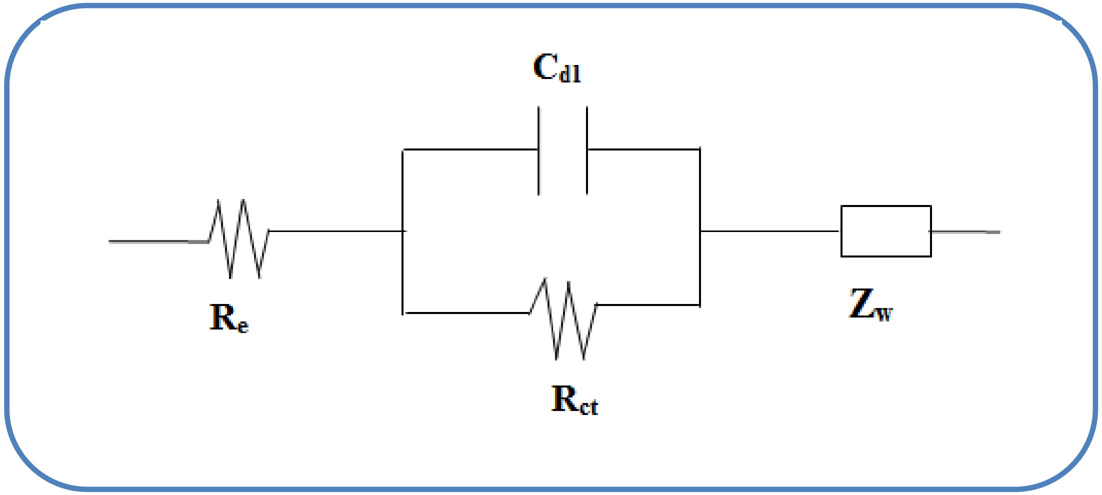
$$Z_w = \frac{\sigma}{\sqrt{\omega}} - j\frac{\sigma}{\sqrt{\omega}}$$

Source: Andreas Jossen, “Fundamentals of battery dynamics” J.Power Sources, vol.154 ,pp.530–538, 2006

Development of Over-potential :Warburg element

Warburg element mainly occurs in electrolyte, it should be in series to the electrochemical charge transfer reaction .

With the consideration of this mixed kinetic and charge transfer control, and equivalent circuit is constructed as below:



Development of Over-potential : Butler-Volmer

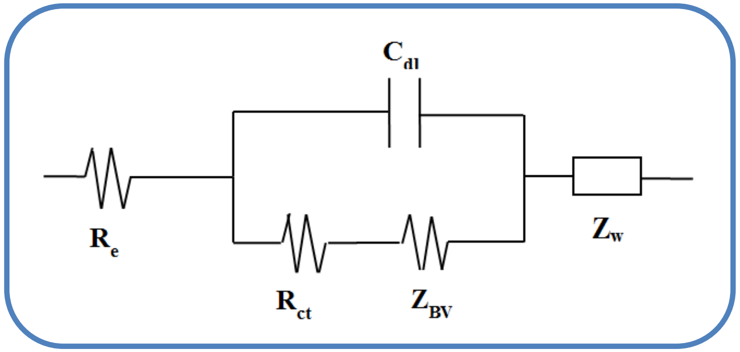
In a continuous discharging operation of battery, reduction in the active mass concentration at the porous electrode will occur. The reduction in the active mass concentration also affects the kinetics of electrochemical reactions at the electrodes, and affects the over-potential.

Such effect can be taken into account by including Butler-Volmer term in our model , and the corresponding impedance presented by this term is given by Shepherd

$$Z_{BV} = k\frac{Q_m}{Q_m - \int idt}$$

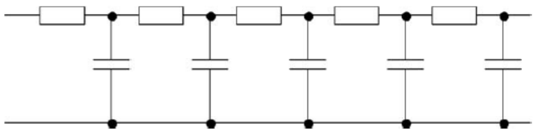
Where K is rate constant for electrode reaction.

Since the Butler-Volmer term accounts for the process at the electrodes, Z_{BV} should be in series with R_{ct}, and therefore the equivalent circuit model for a Li Ion cell is as shown in below:

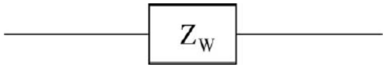


Cource: C.M. Shepherd, “1965 Design of Primary and Secondary Cells An Equation Describing Battery Discharge” J.Electrochem. Soc, vol. 112, pp. 657-664, 1965

Development of Over-potential : Temporal model



Electric equivalent circuit for diffusion effects.



Electric equivalent circuit for diffusion effects.

- Through the inverse Laplace transform of Warburg impedance, the expression is shown below:

$$Z_\omega = \sum_{n=1}^{\infty} \frac{1}{C_\omega} exp \frac{-t}{R_n C_\omega}$$

and

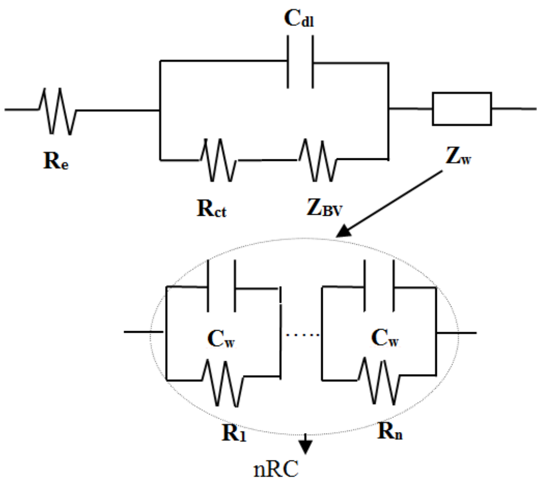
$$R_n = \frac{8k_1}{(2n-1)^2 \pi^2}$$

$$C_\omega = \frac{k1}{2k_2^2}$$

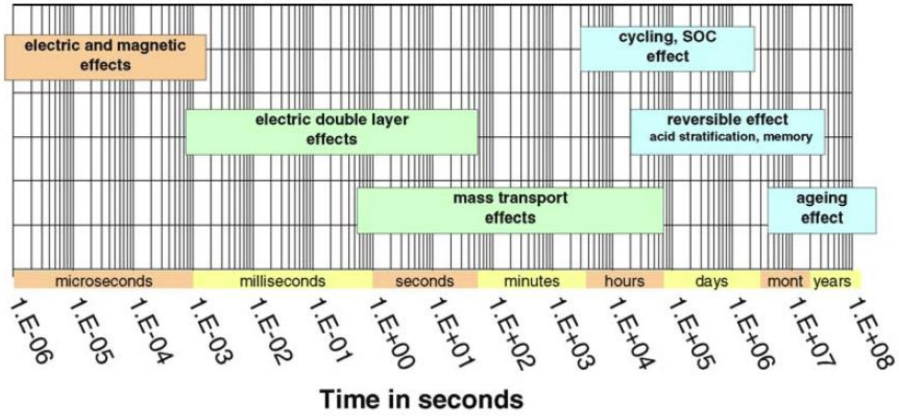
Source: E. Kuhn, C. Forgez, G. Friedrich, “Electric Equivalent circuit of a NiMH Cell, Methods and results,” EVS 20, Long Beach, CA, 2003

Development of Over-potential : Temporal model

- The equivalent circuit shown in below:

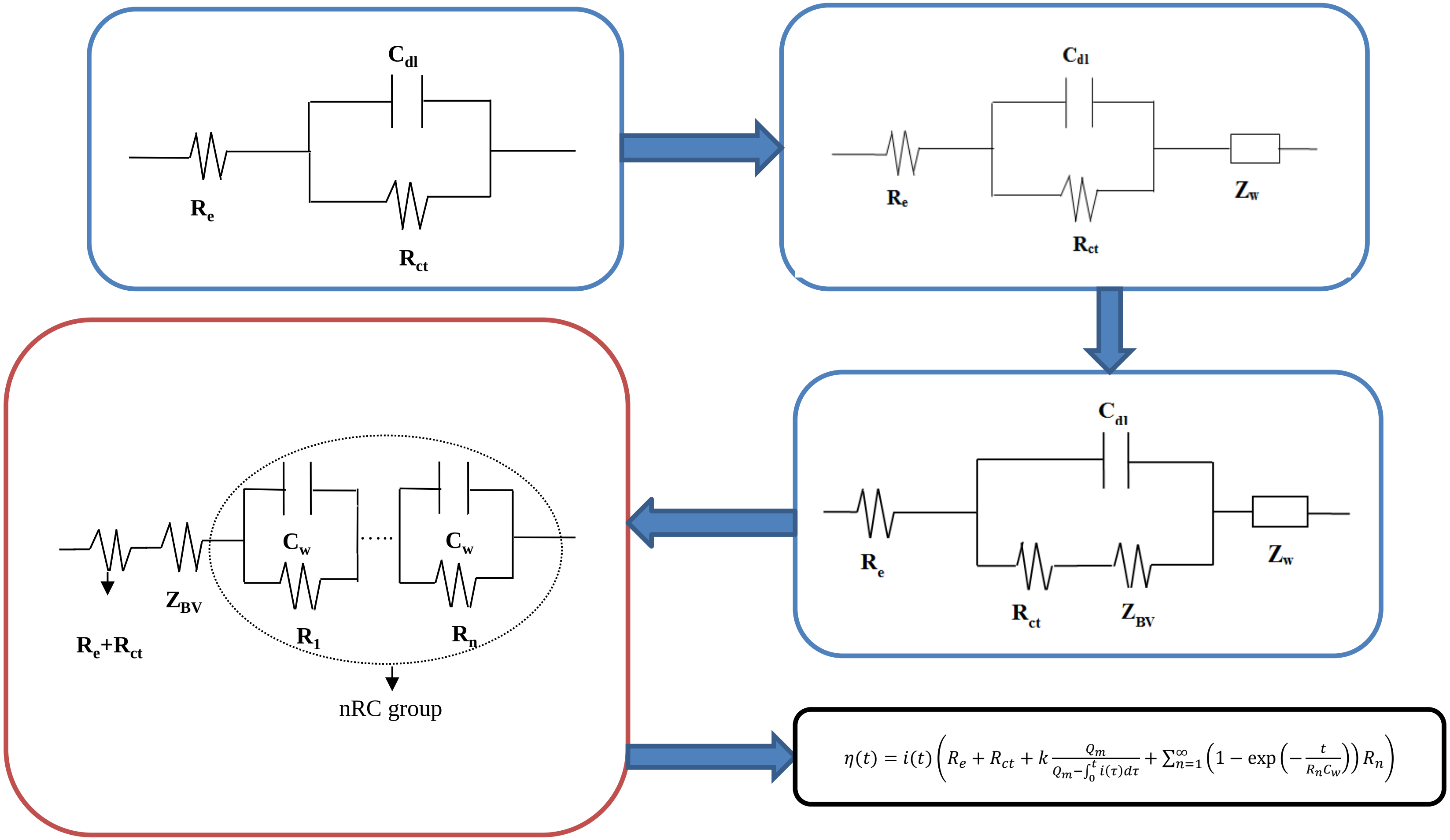


- It is too complex for obtaining time domain relationship between the terminal voltage and discharging current of the cell.



- Since the time constant due to C_{dl} (in the order of 10^{-3} milliseconds to 10 seconds)is much smaller than that due to the Warburg element and the Butlet-Volmer term (in the order of 1 second to 10^5hours) and in our case the initial exponential decay is just 0.03 second of the discharging curve is omitted, and use the circuit is simplified without C_{dl}

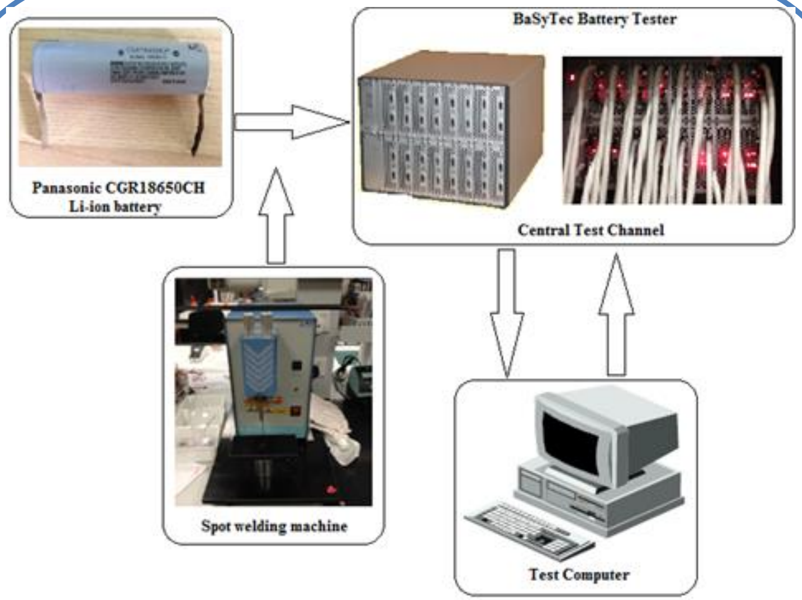
Development of Over-potential

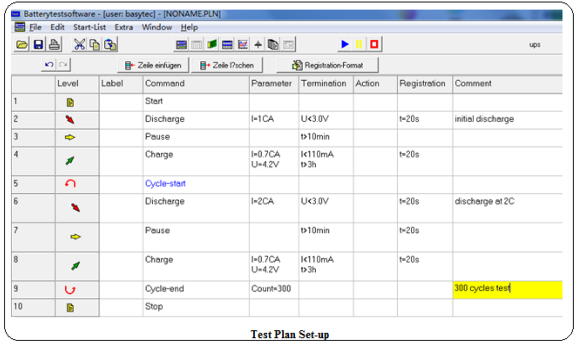


$$\eta(t) = i(t)\left(R_e + R_{ct} + k\frac{Q_m}{Q_m - \int_0^t i(\tau)d\tau} + \sum_{n=1}^{\infty}\left(1 - \exp\left(-\frac{t}{R_n C_w}\right)\right)R_n\right)$$

Model Verification

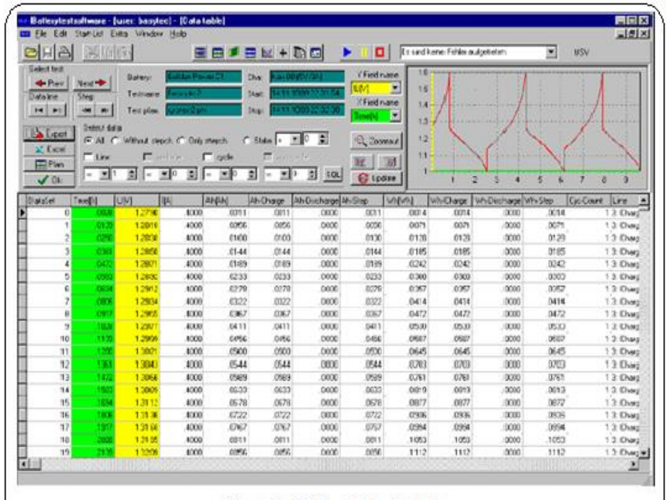
Experimentation: Hardware set-up





	Level	Label	Command	Parameter	Termination	Action	Registration	Comment
1			Start					
2			Discharge	I=1CA	U<3.0V		t=20s	initial discharge
3			Pause		t>10min			
4			Charge	I=0.7CA U=4.2V	I<110mA t>3h		t=20s	
5			Cycle-start					
6			Discharge	I=2CA	U<3.0V		t=20s	discharge at 2C
7			Pause		t>10min		t=20s	
8			Charge	I=0.7CA U=4.2V	I<110mA t>3h		t=20s	
9			Cycle-end	Count=300				300 cycles test
10			Stop					

Test Plan Set-up



Numerically Test Data Analysis

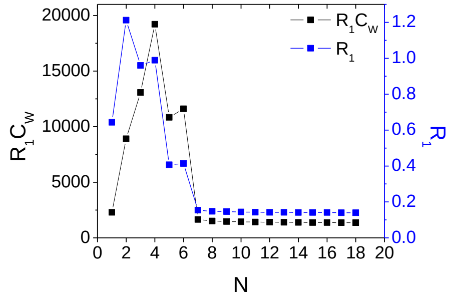
Battery	Characteristics
Series	Panasonic Solid Solution (PPS)
Chemical System	$LiNiMnCoO_2$ (NMC)
Nominal voltage	3.6V
Capacity	2,250mAh Typical
Charging Condition	CVCC 4.2V max.0.7 C-rate (1500mA), 110mA cut-off 25 ° C
Discharging Condition	CONSTANT CURRENT, 3.0V cut-off 25 ° C
Max discharge current	10A (25 ° C)
Diameter(with tube)/Max.	18.6 (mm)
Height(with tube)/Max	65.2 (mm)
Approx.Weight	44 (g)

Table 1 CGR18650CH Li-ion battery specification

Warburg Element

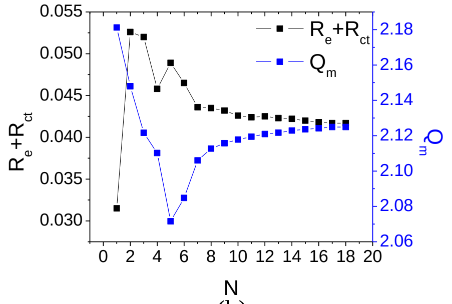
Table 2 Estimation of battery discharging model's parameters for different number of RC groups

n	$R_1(\Omega)$	$R_1C_w(s)$	Re+Rct(Ω)	$Q_m(C)$	m_1	m_2	k(Ω)	α	β	rmse(V)
1	0.643	2298	0.0315	2.1812	1.0	0.5	0.0028	3.955	1.0989	0.0045
2	1.212	8915	0.0526	2.1480	1.0	0.5	0.0016	4.047	0.9737	0.0053
3	0.960	13075	0.0520	2.1216	1.0	0.5	0.0009	4.043	0.5155	0.0064
4	0.989	19211	0.0458	2.1102	1.0	0.5	0.0006	4.014	0.3761	0.0069
5	0.407	10837	0.0489	2.0716	1.0	0.5	0.0000	4.029	0.0001	0.0106
6	0.414	11606	0.0465	2.0848	1.0	0.5	0.0002	4.026	0.0002	0.0110
7	0.154	1653	0.0436	2.1060	1.0	0.5	0.0005	4.057	0.0000	0.0134
8	0.148	1518	0.0435	2.1127	1.0	0.5	0.0006	4.062	0.0000	0.0136
9	0.146	1473	0.0432	2.1157	1.0	0.5	0.0007	4.062	0.0000	0.0137
10	0.144	1445	0.0426	2.1178	1.0	0.5	0.0007	4.062	0.0000	0.0139
11	0.143	1426	0.0424	2.1194	1.0	0.5	0.0007	4.063	0.0000	0.0140
12	0.142	1409	0.0425	2.1209	1.0	0.5	0.0008	4.064	0.0000	0.0140
13	0.142	1400	0.0423	2.1217	1.0	0.5	0.0008	4.064	0.0000	0.0141
14	0.141	1387	0.0422	2.1229	1.0	0.5	0.0008	4.065	0.0000	0.0142
15	0.141	1380	0.0420	2.1236	1.0	0.5	0.0008	4.065	0.0000	0.0142
16	0.141	1376	0.0418	2.1242	1.0	0.5	0.0008	4.065	0.0000	0.0143
17	0.140	1369	0.0417	2.1249	1.0	0.5	0.0008	4.065	0.0000	0.0143
18	0.140	1369	0.0417	2.1249	1.0	0.5	0.0008	4.065	0.0000	0.0143



(a)

Fig.8(a). Variation of *R1*and *R1Cw*with different value of n

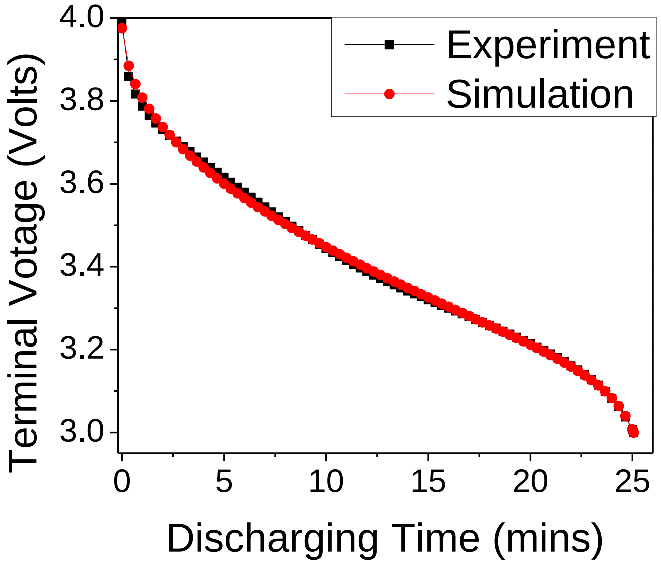


(b)

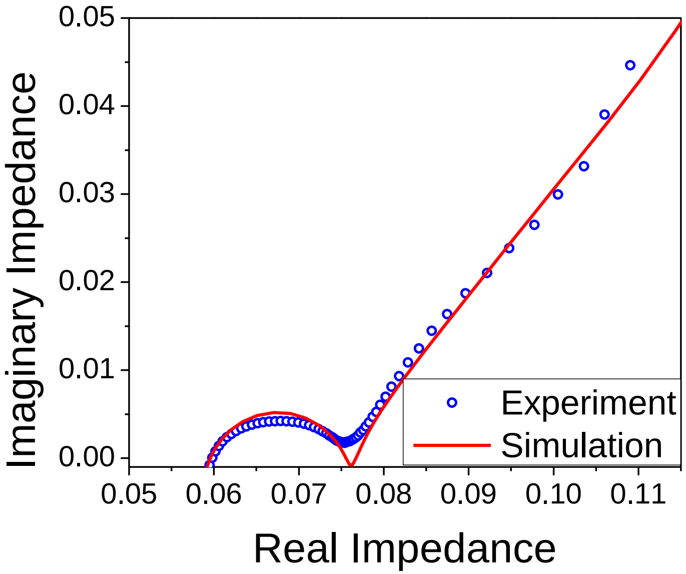
Fig.8(b). Variation of Re+Rct and *Qm* with different value of n

Table 3 Estimation of battery discharging model's parameters using 15 of RC group for the Warburg elements

N	$R_1(\Omega)$	$R_1C_w(s)$	Re+Rct(Ω)	$Q_m(C)$	m_1	m_2	k(Ω)	α	β	rmse(V)	Accuracy
15	0.141	1380	0.042	2.1236	1.0	0.5	0.0008	4.065	0	0.0142	0.9964



Discharging curve of Panasonic CGR18650CH Li-ion battery at 2C under Lab's ambient temperature of 23^{o}C until the terminal voltage drop to cut-off voltage of 3V



Comparison of Experimental and computed EIS spectrum of our Li Ion cell at 4V OCV

Our model is derived based on the physical chemistry processes in the battery discharging process. The result shows same experimental EIS spectrum with the parameters as determined from the discharging curve.

Experiment: Effect of Resting time

- In order to obtain stable terminal voltage of Li-ion battery, a rest period of at least 12 hours after the battery is fully charged is specified, i.e. the battery can start to discharge only after the rest period. The purpose of the rest period is to regain the chemical equilibrium at the electrodes and compensates for the self-discharge after charging[1].
- A cell is discharged at 2C-rates with different rest time (10mins, 30mins, 1hr, 6hrs and 12hrs) after it is fully charged.

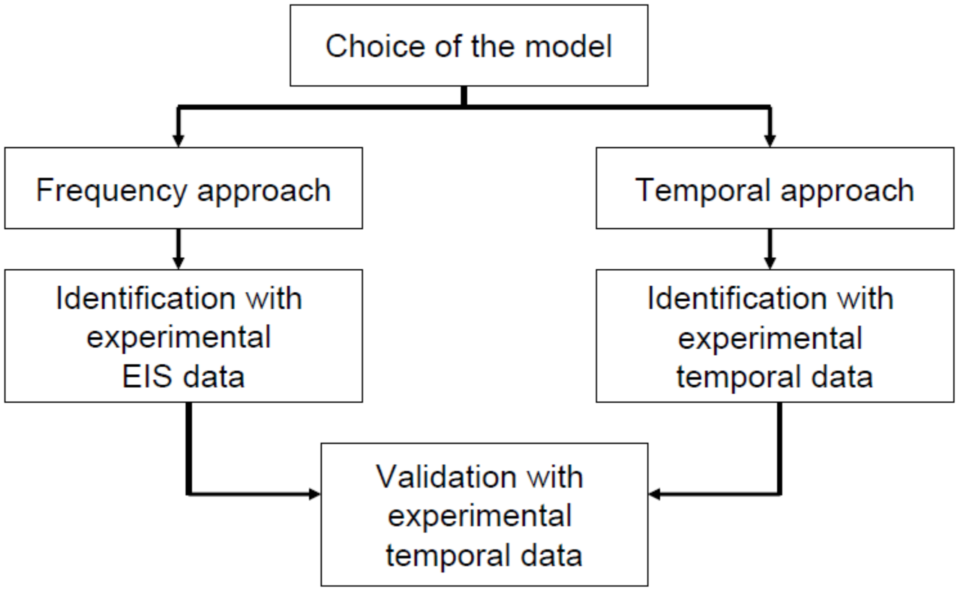
Table 4 Estimation of battery discharging model's parameters at different rest time condition

Rest time	$R_1(\Omega)$	$R_1C_w(s)$	$k(\Omega)$	$Q_m(C)$	m_1	m_2	rmse(V)	Accuracy
10'	0.323	8252	0.0012	2.19	1.0	0.5	0.0120	0.9973
30'	0.315	8259	0.0013	2.18	1.0	0.5	0.0122	0.9972
1h	0.315	8165	0.0011	2.17	1.0	0.5	0.0129	0.9969
6h	0.315	8187	0.0014	2.17	1.0	0.5	0.0116	0.9960
12h	0.315	8184	0.0016	2.17	1.0	0.5	0.0114	0.9966

***Warburg coefficient is main contributor**

Source: Isidor Buchmann, *Batteries in a Portable World* - A Handbook on Rechargeable Batteries for Non-Engineers-3rd Edition. Cadex Electronics Inc. 2011

Battery modeling : overview



Choice of the model

Frequency approach

Temporal approach

Identification with experimental EIS data

Identification with experimental temporal data

Validation with experimental temporal data

*****We find a path to mix this two approaches, and make it possible to monitoring and characterizing of Lithium-ion batteries ageing on line!!!**

Source: Serge.pelissier,“Battery for electric and hybrid vehicles state of the art,” *IEEE. VPPC*, Lille, FR, 2010, Tutorial 2-2 part.2

Experiment: Effect of Discharging Current

- **We conduct experiments with discharging current of 1C, 1.5C and 2C to examine the impact of the discharging current on the model parameters. The results are shown in Table 5**

Table 5 Model Parameters determined from discharging curves at different discharging currents

Discharging Current	$R_1(\Omega)$	$R_1C_w(s)$	$k(\Omega)$	$Q_m(C)$	m_1	m_2	rmse(V)	Accuracy
2C	0.140	1360.65	0.000874	2.13	1	0.5	0.0144	0.996
1.5C	0.159	1533.19	0.000108	2.18	1	0.5	0.0148	0.996
1C	0.175	2045.91	0.000176	2.17	1	0.5	0.0153	0.996

- **Larger discharging current => the diffusion of the ionic species to move faster in the electrolyte => Warburg element will be smaller as show in Table 5**
- **Larger discharging current => too many charges arriving at the negative electrode per unit time => render inefficient storage of charges=> apparent Qm smaller**

Experiment: Effect of Changing Discharging Current

- **Since discharging current affect the model parameters, we use the values in Table 5 to determine the discharge curve of our battery cell with step change in the discharging current, with 30 minutes in between the step change.**

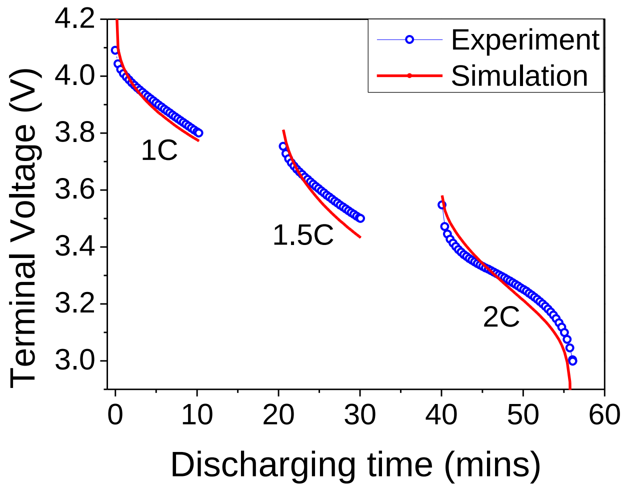
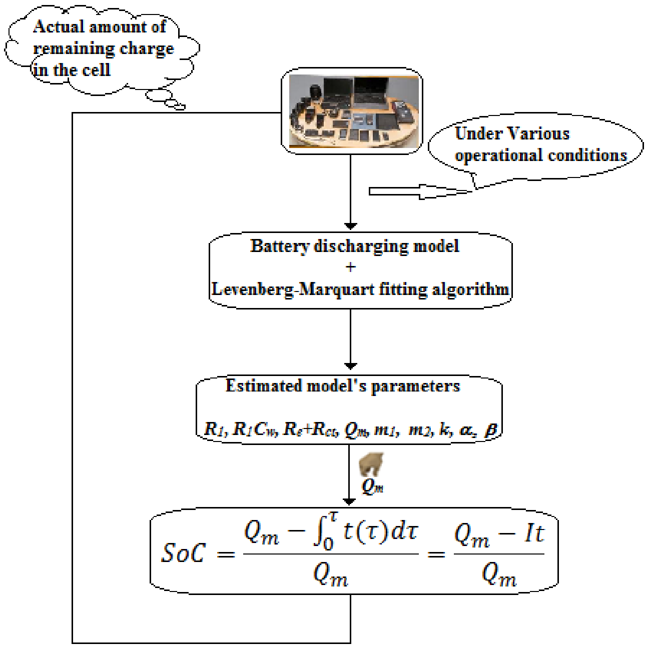


Fig.10. Comparison of our computed and experimental discharging curve

*****The maximum error in the battery voltage is 0.0808V and the root mean square error in the battery voltage is only 0.0326V, which is very small. The larger deviation occur at lower battery voltage (or correspondingly lower SoC) is due possibly to the fact that our model assumption is for SoC>50%!**

Application of the Battery Model

- **This method is fast and accurate, taking approximately 0.3011s , and can easily be implemented in most practical applications.**



$$SoC = \frac{Q_m - \int_0^{\tau} t(\tau)d\tau}{Q_m} = \frac{Q_m - It}{Q_m}$$

Fig.11. An implementation flow-chart of SoC estimation

“A Practical Framework of electrical based On-line SoC Estimation of Lithium-Ion Battery”, Journal of power source, F Leng, CM, Tan, R Yazami, MD, Le (under review)

Model : Limitation

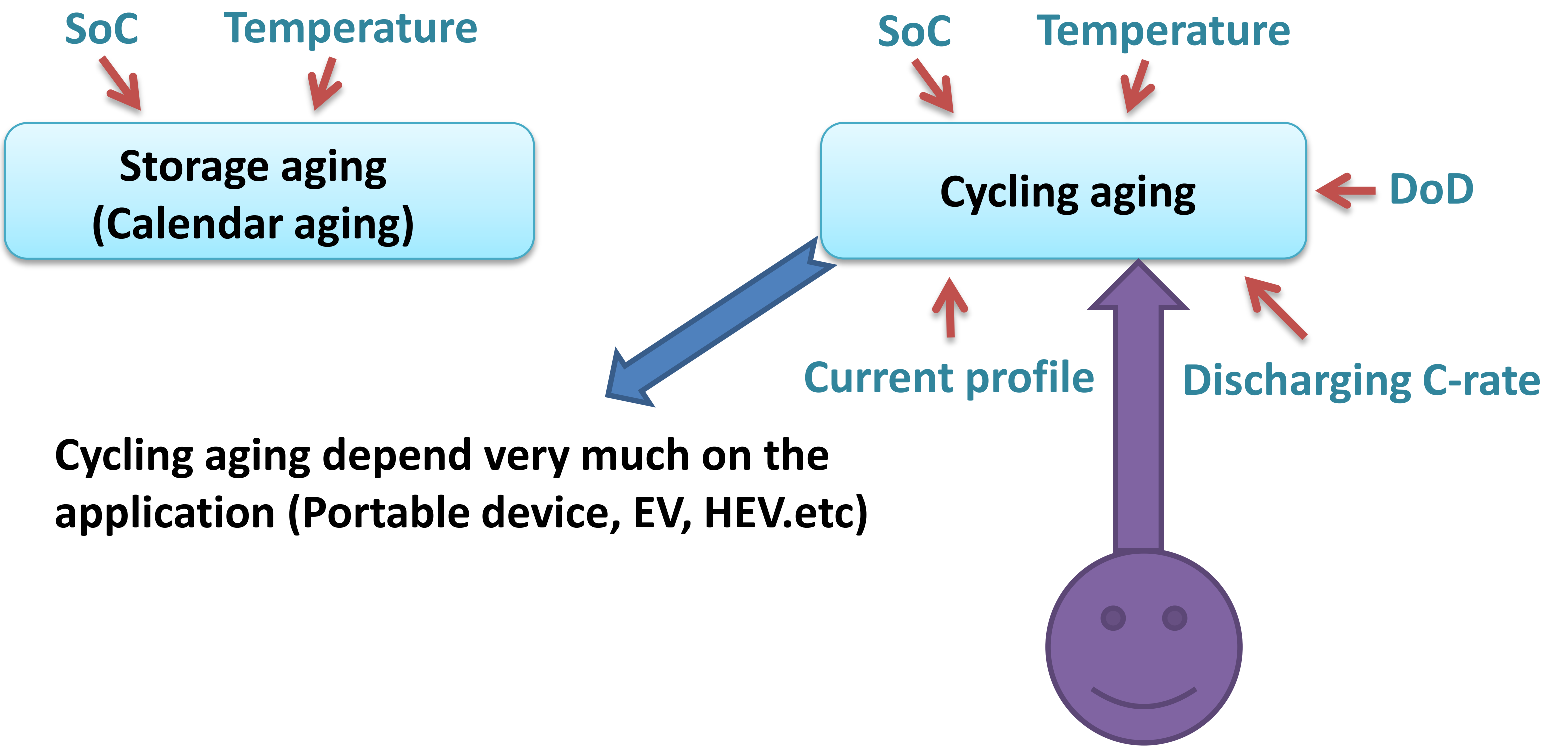
As this is a first attempt to relate the electrochemical process in Li-Ion battery to the components in electrical , we limit our study to the following situation:

- The self-discharge behavior of the battery is not considered. This can be considered only if the physical-chemistry process of the self-discharge is well understood.
- The temperature of the battery during discharging is assumed to be constant. The model in this work can in principle be extended to include the temperature effect by making the components in the equivalent circuit to be temperature dependent. This will be considered in our future work with experimental data.
- SoC is always above 50% for practical consideration. Extension to SoC all the way to 20% will be considered in future.
- No high discharging current so that Peukert effect is insignificant.

Characterization of battery Aging

Aging Introduction:

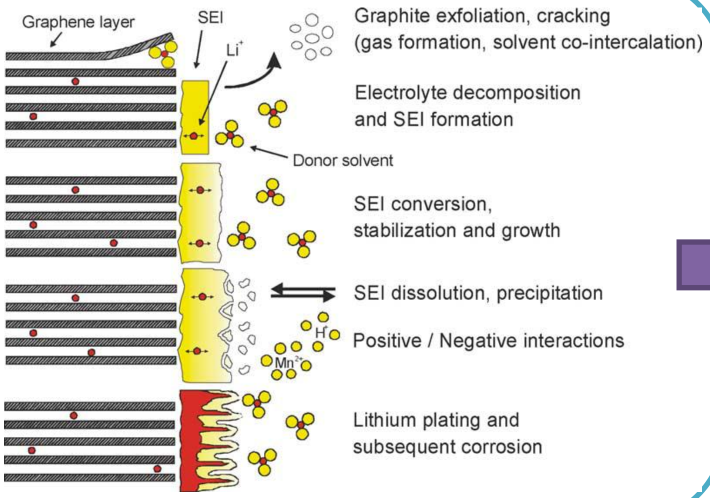
Aging = irreversible damage to battery , and hence loss of performances

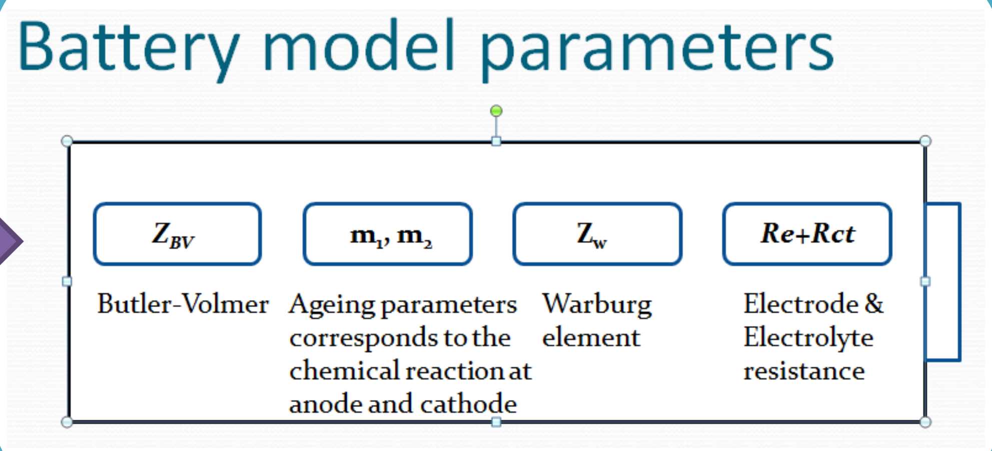


Cycling aging depend very much on the application (Portable device, EV, HEV.etc)

Lithium-ion battery main ageing mechanisms:

Cause	Electrolyte decomposition (SEI formation)	Solvent co-intercalation, gas evolution and subsequent cracking formation in particles	Decrease of accessible surface area due to continuous SEI growth	Changes in porosity due to volume changes, SEI formation and growth	Contact loss of active material particles due to volume changes during cycling
Effect	• Loss of lithium • impedance rise	• Loss of active material (graphite exfoliation) • Loss of lithium	• Impedance rise	• Impedance rise	• Loss of active material





Battery model parameters

Z_{BV}	m_1, m_2	Z_w	$Re+Rct$
Butler-Volmer	Ageing parameters corresponds to the chemical reaction at anode and cathode	Warburg element	Electrode & Electrolyte resistance

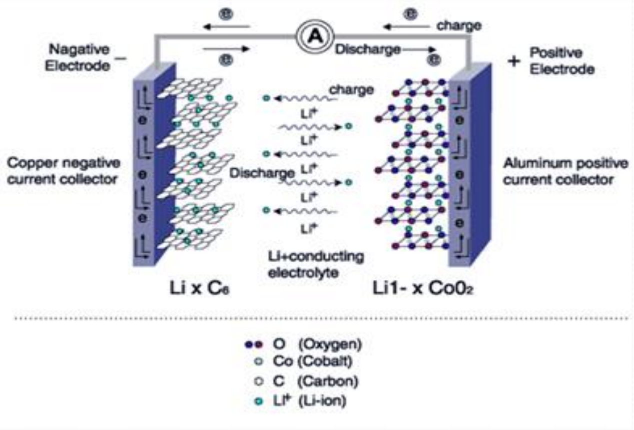
- J. Vetter, M. Winter, M. Wohlfahrt-Mehrens "ageing mechanisms in Lithium-ion batteries", J.Electrochem. Soc, Vol.154, No.8, pp.393-403, 2009

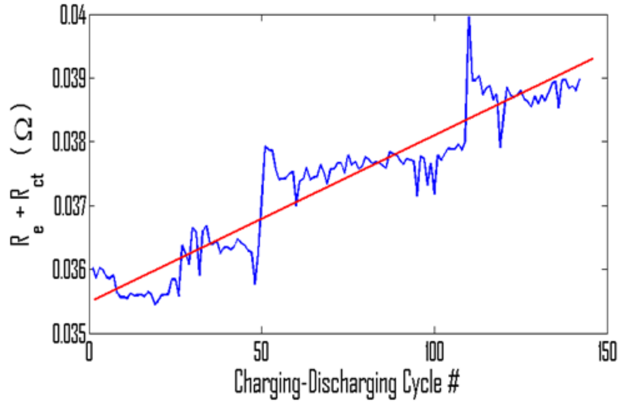
Design of aging tests:

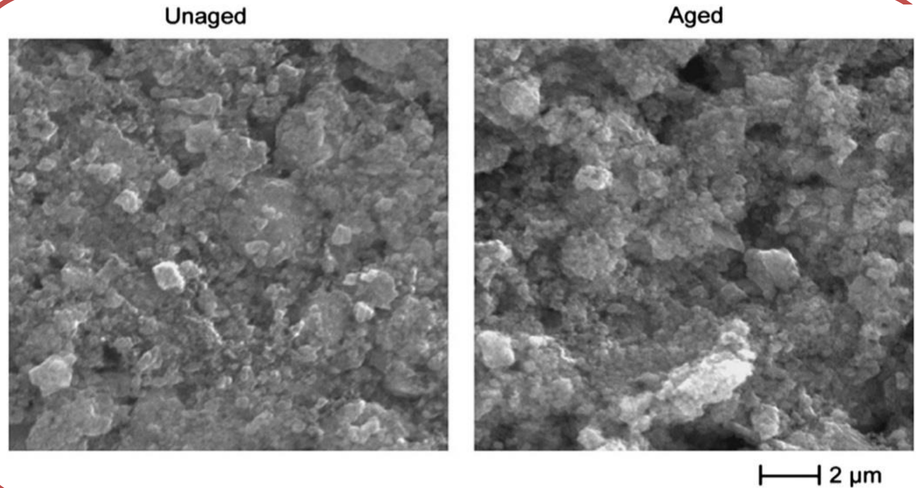
Our Cycling Test:

- **The charging process is carried out at a fixed charging rate of 0.7C in CC mode and a voltage of 4.2V in CV mode with a charge-termination current of 110mA, according to the company specification. Since this work focus only on the discharging process, the charging condition is fixed for all cases.**
- **Cycling the battery under constant ambient temperature and fixed constant discharging C-rate (1C, 1.5C and 2C) to the cut-off voltage of 3V as shown in the battery specification**

Electrode/Electrolyte Interface degradation



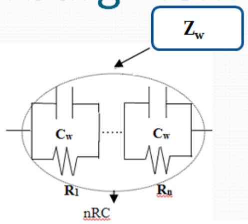


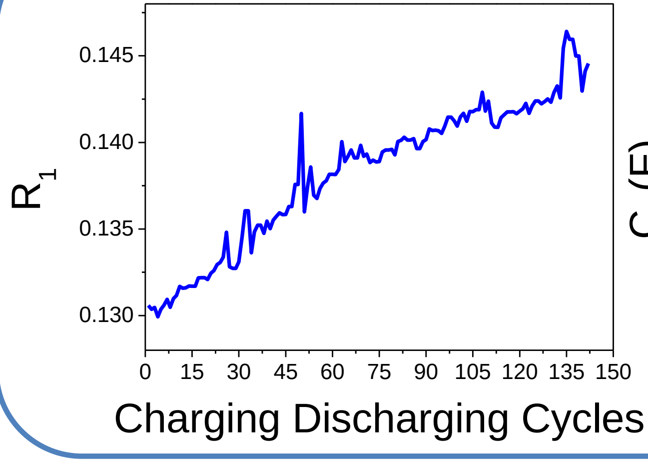


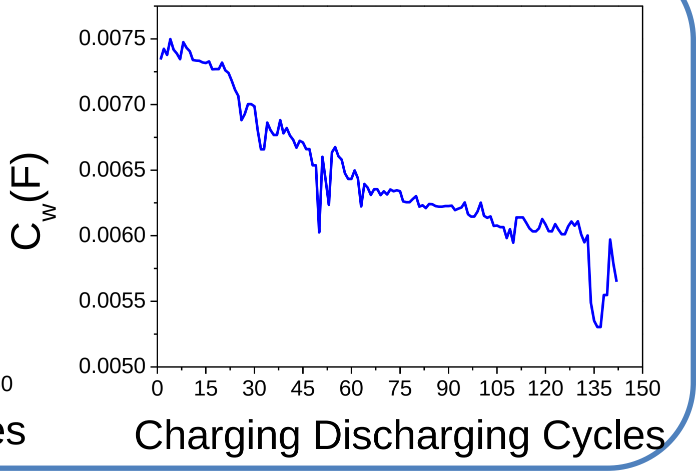
Source: Samartha A. Channagiri, Shrikant C. Nagpure, S.S. Babu, Garret J. Noble, Richard T. Hart "Porosity and phase fraction evolution with aging in lithium ion phosphate batter cathode" J.Power Sources, vol.243 ,pp.750 - 757, 2013.

Electrolyte degradation

Warburg Element

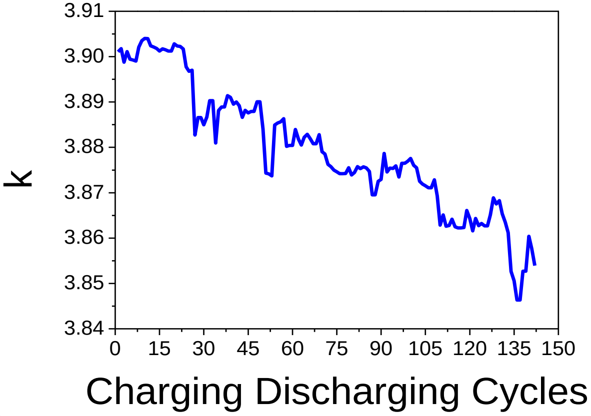






Butler-Volmer

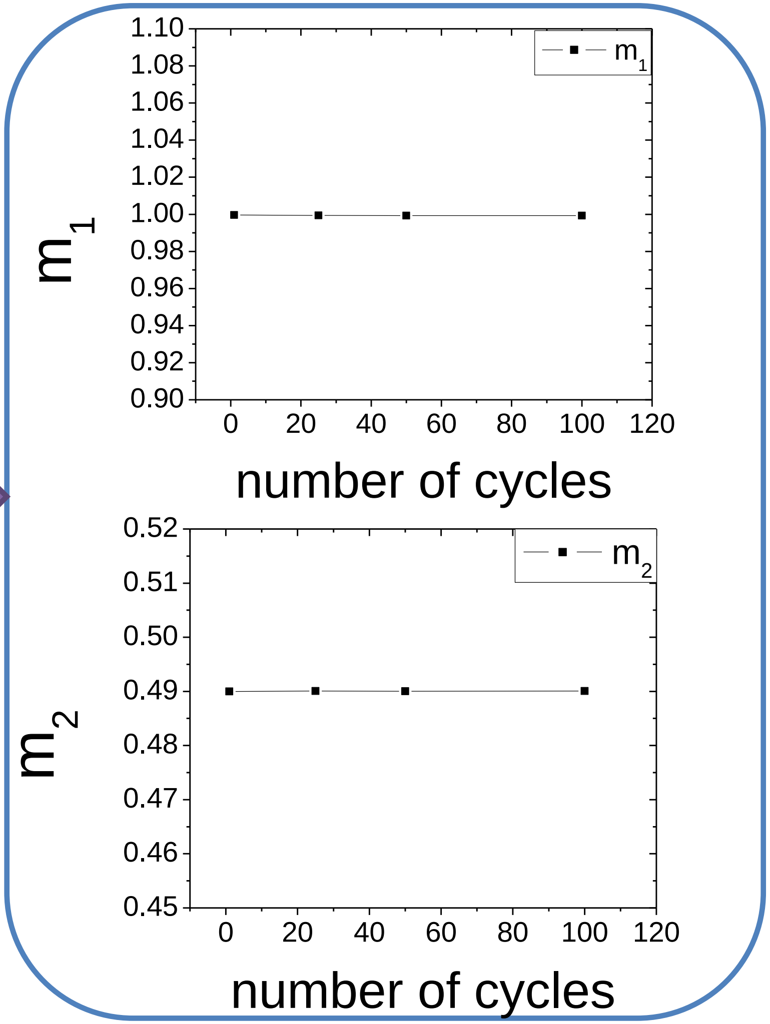
$$Z_{BV} = k\frac{Q_m}{Q_m - \int i\,dt}$$



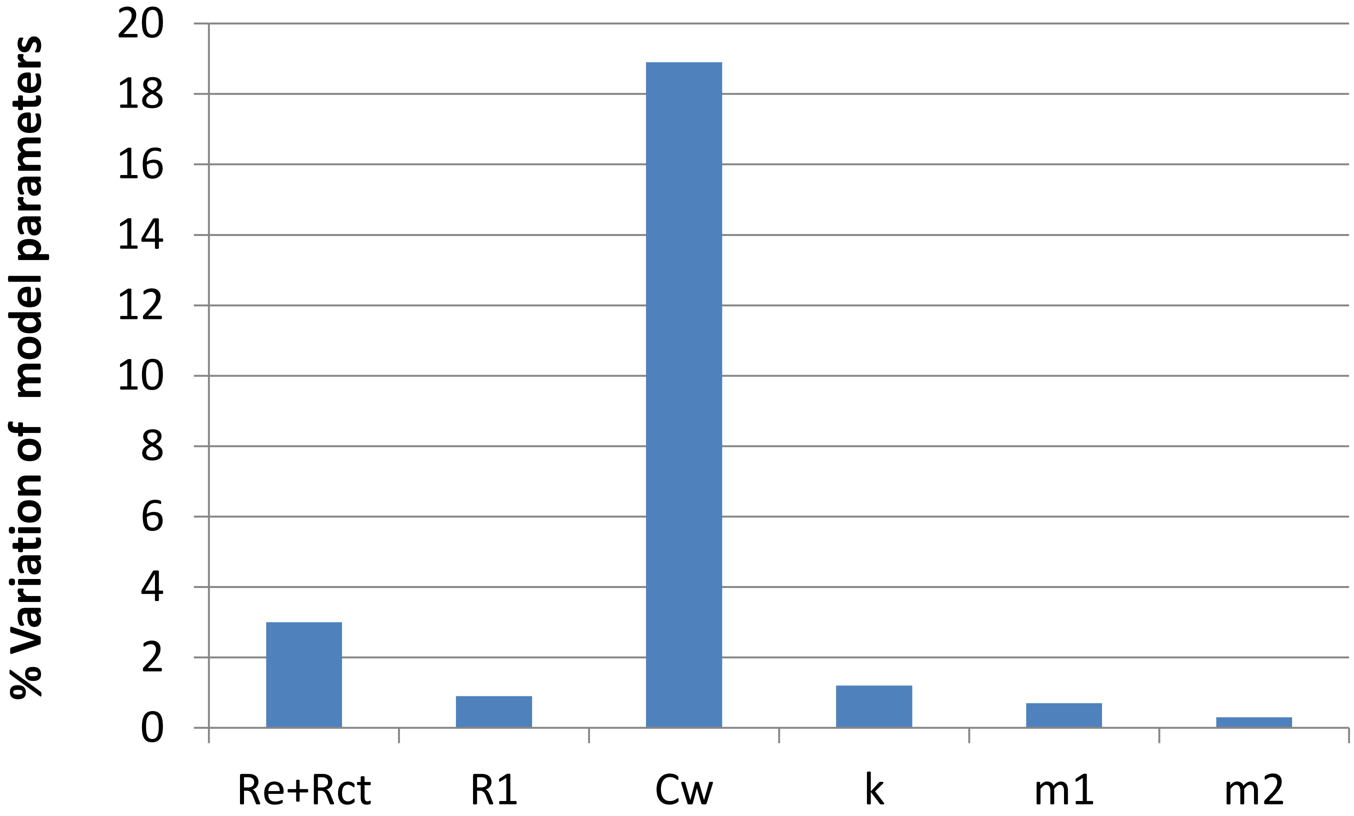
Electrode degradation

$$Q_{max}^{+} = m_1 Q_m \, , m_1 \leq 1 \; ,$$

$$Q_{max}^{-} = m_2 Q_m \; , m_2 \leq \frac{1}{2} \; ;$$



The rate of change of different model parameters that correspond to different ageing mechanisms



In-situ time domain characterization method

Different test conditions (Factors of ageing)

Constant discharging
Discharging C-rate

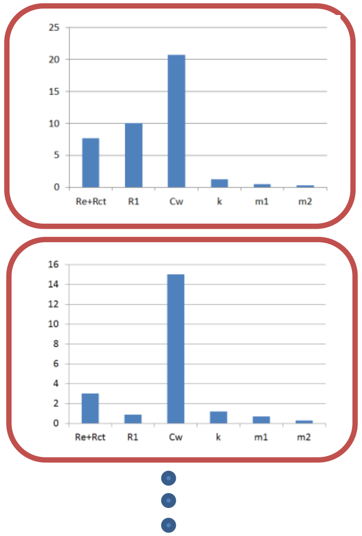
Temperature

DoD

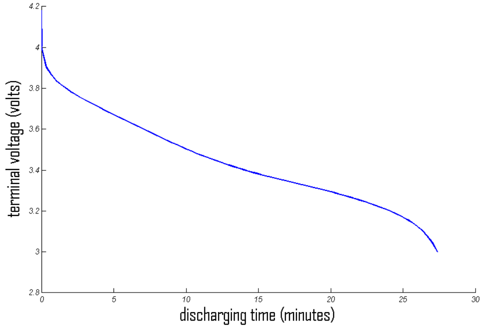
Application

Current Profile

Different ageing characteristics



Discharging curve



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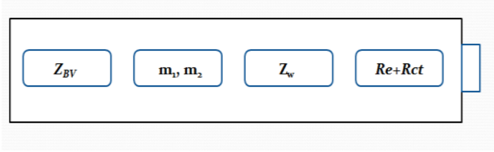
Proposed battery model



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Conclusion

- An electrical model is developed in this work, and it can determine Q_m easily after every discharge cycle, making the estimation of SoH and SoC using Coulomb counting method more accurate.
- This electrical model is able to provide an in-situ time-domain characterization method that enables us to monitor the different aging mechanisms under various operating conditions on-line through its discharge curve alone, and identify the dominant degradation mechanisms.
- The rate of aging through SoH determination allows estimation of the Remain Useful Lifetime (RUL).

Thank you

Q & A

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