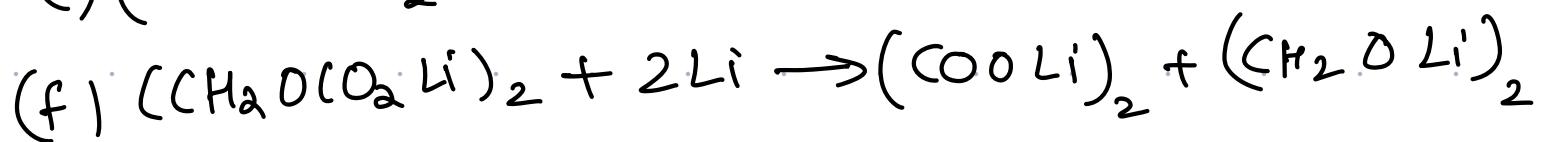
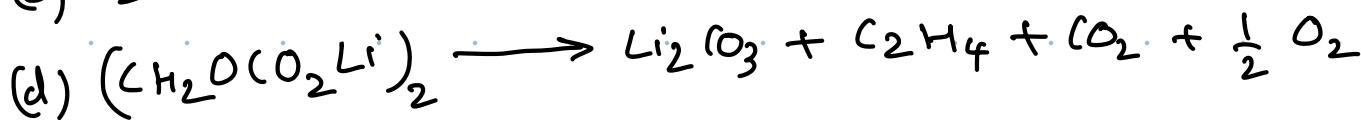
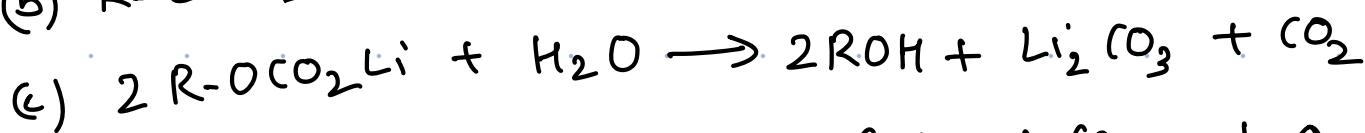
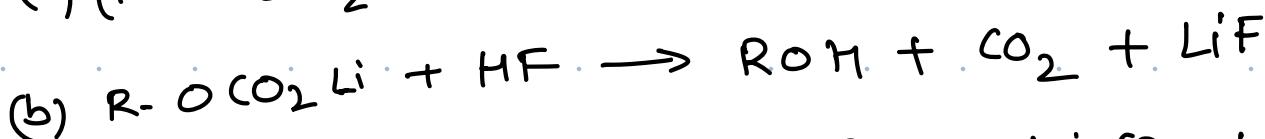
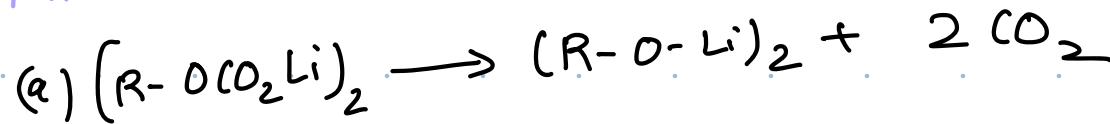


(I) All possible reactions based on literature

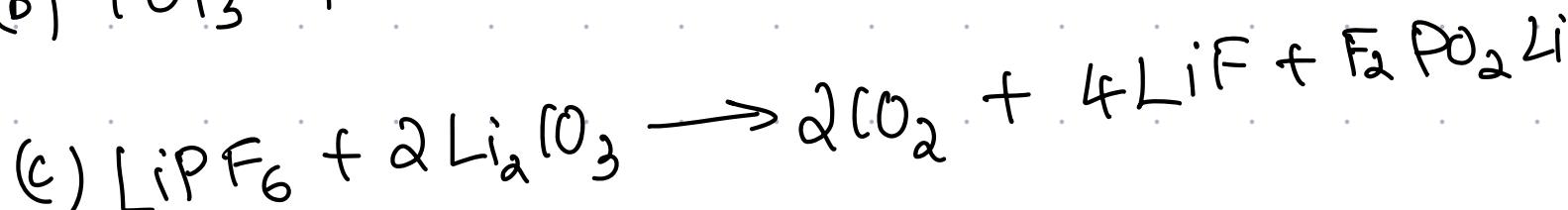
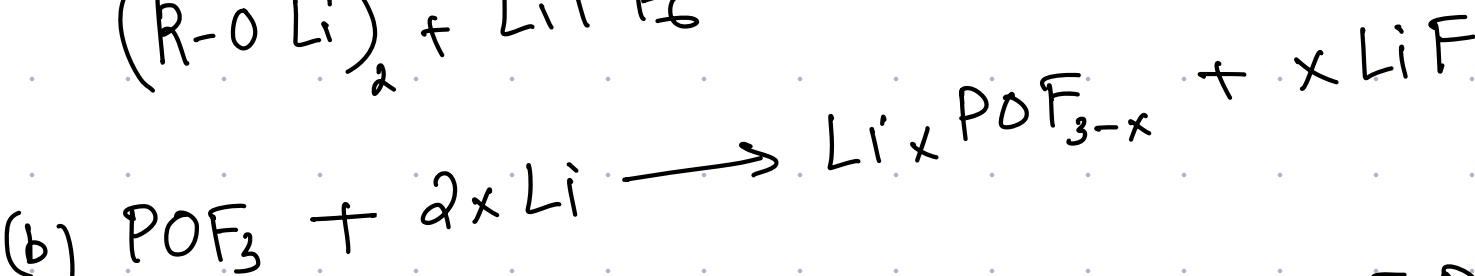
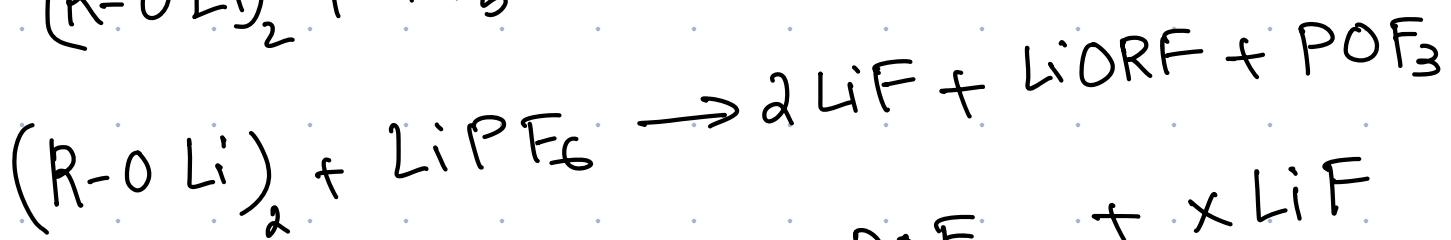
(I.1) Involving primary SEI

Primary SEI \rightarrow SEI developed during the cycling.



(I.2) involving secondary SEI @ the elevated temp.

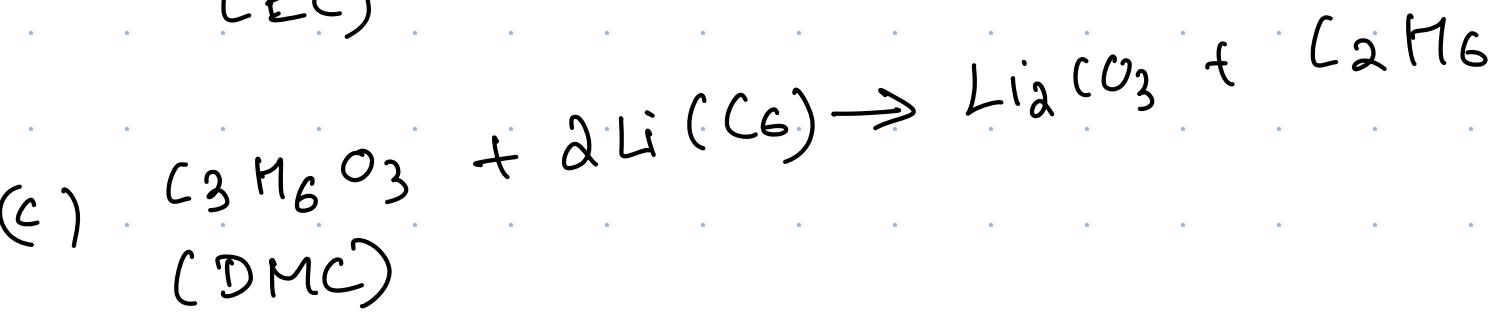
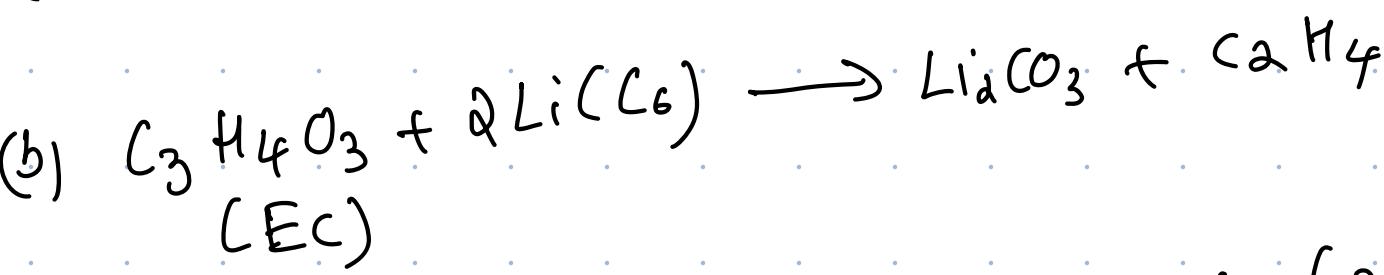
Secondary SEI \rightarrow Forms @ beginning of TR.



(1.3) Between Li (anode) and solvent in electrolyte

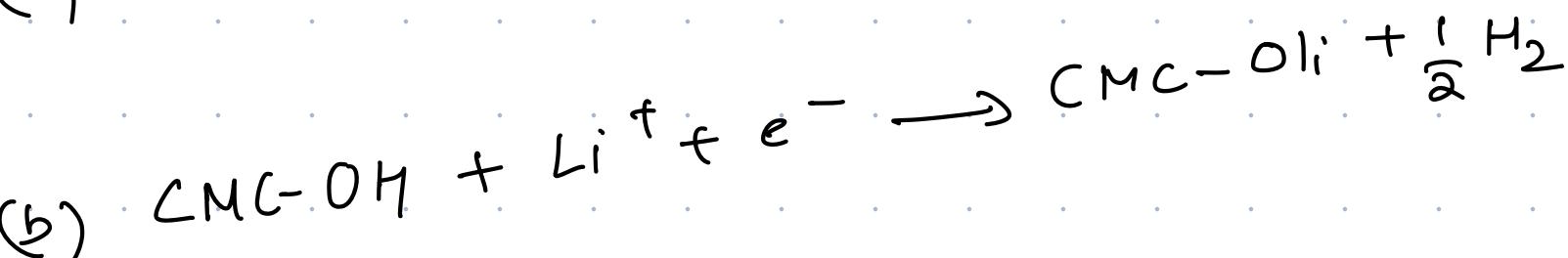
Solvents \Rightarrow EC {ethylene carbonate}

\Rightarrow DMC {dimethyl carbonate}



(1.4) Reactions of Binder (CMC)

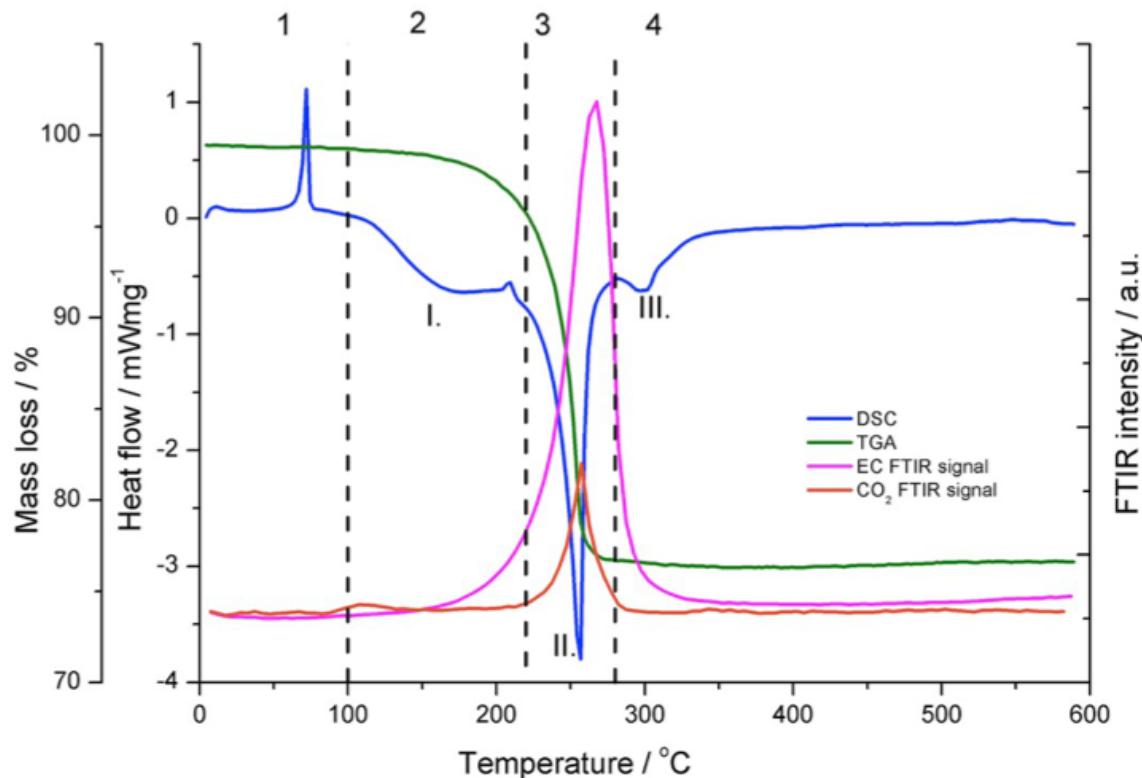
Binder \Rightarrow CMC (carboxymethyl cellulose)



(2) Observed DSC curve

Jour

(a)



Key points

- * Only blue curve important for us
- * Blue curve = DSC curves [measures heat flow from anode + electrolyte when heated to temp given in x axis]
- * 4 regions
- Region I $\rightarrow T < 100^\circ\text{C}$

\Rightarrow One endothermic peak

\Rightarrow No gas formation

\Rightarrow No influence on Thermal Runaway

\Rightarrow Ignored in analysis & kinetic

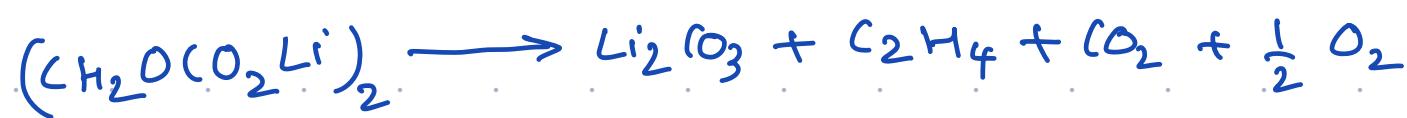
modeling

\Rightarrow $100 \text{ L} \leq T \leq 200^\circ\text{C}$

\Rightarrow Peak I \nearrow (Exothermic)

\Rightarrow The region 2 exothermic heat comes from the following reactions

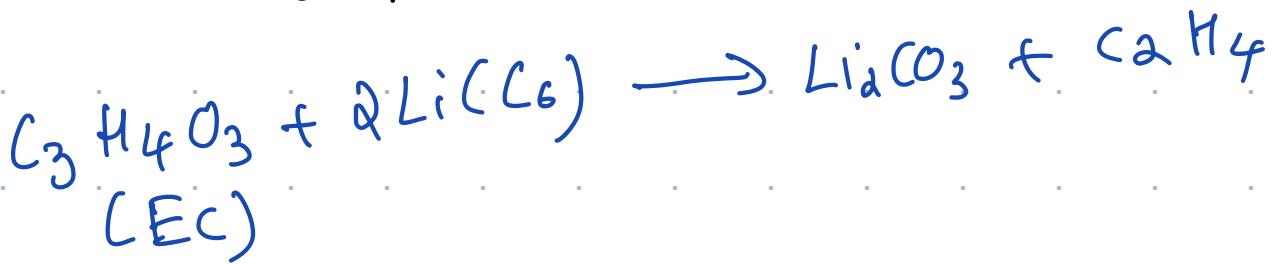
(1) SEI decomposition with gas evolution



(2) SEI decomposition with Lithium



(3) Lithiated graphite reaction with electrolyte



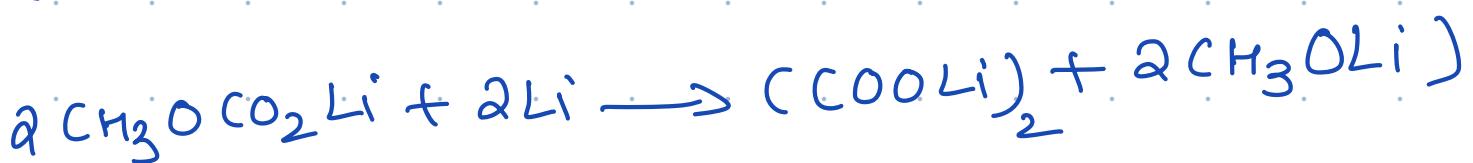
(4) SEI decomposition with CO_2 evolution



(5) SEI interaction with HF / H_2O



(6) SEI transformation w/o any gas evolution



Key points

* Reactions (1-3) was supposed to generate a lot of gas (as per stoichiometry)

↓
FTIR & GC show very less gas

↓
Hence, Rxns (1 - 3) are not happening
as written in literature

↓
These reactions are ignored in the
heatflow of region 2

* Based on experiment, reactions (4 - 6) are
consistent & correct

* Absence of gas evolution suggests that SEI

is not disintegrating, but undergoing transformation

↓
XRD shows lithium content in graphite is
reducing (b/w $110^{\circ}\text{C} - 200^{\circ}\text{C}$); so, lithium
is reacting to form secondary SEI

* We choose only reaction 6 in kinetic
Model; because

→ No gas evolution → less mass loss
→ gradual consumption of Lithium
(gradual ⇒ Broad exothermic peak ⇒ consistent)



Implications to be considered in model

→ SEI transformation = SEI thickening

Region 2 ⇒ Exothermic reaction of peak 1

* SEI transformation w/o any gas evolution



* Kinetic Model for CRNN

Some observations

* The reaction do not follow Arrhenius eqns

* When heating rate ↑; reaction occurs @ lower temp → Not a characteristic of Arrhenius

* When heating rate ↑; peak width ↓
(Peak narrowing)

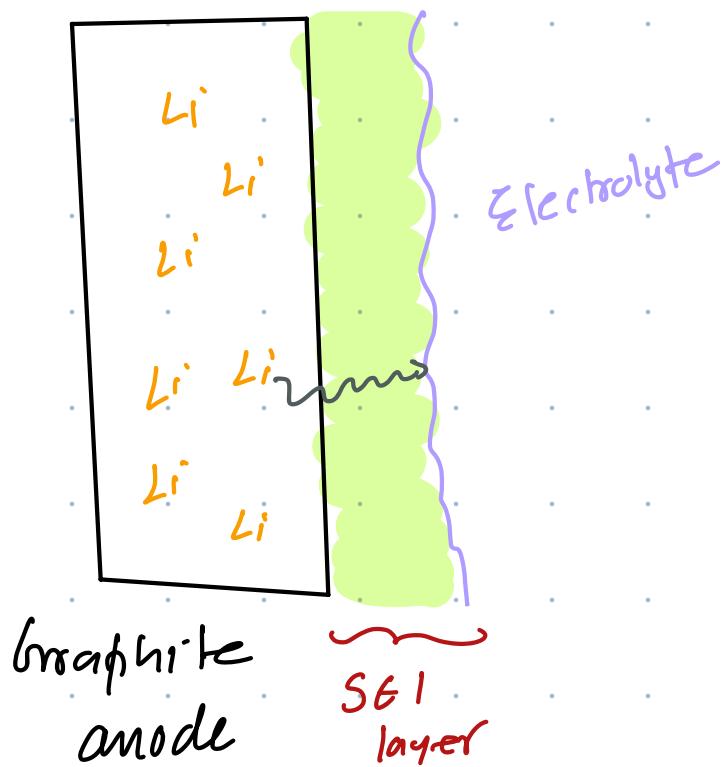
Faster rxn @ higher heating rate

* New model \Rightarrow Diffusion-type Kinetic model

Region 2, peak 1 \Rightarrow Due to SEI transformation

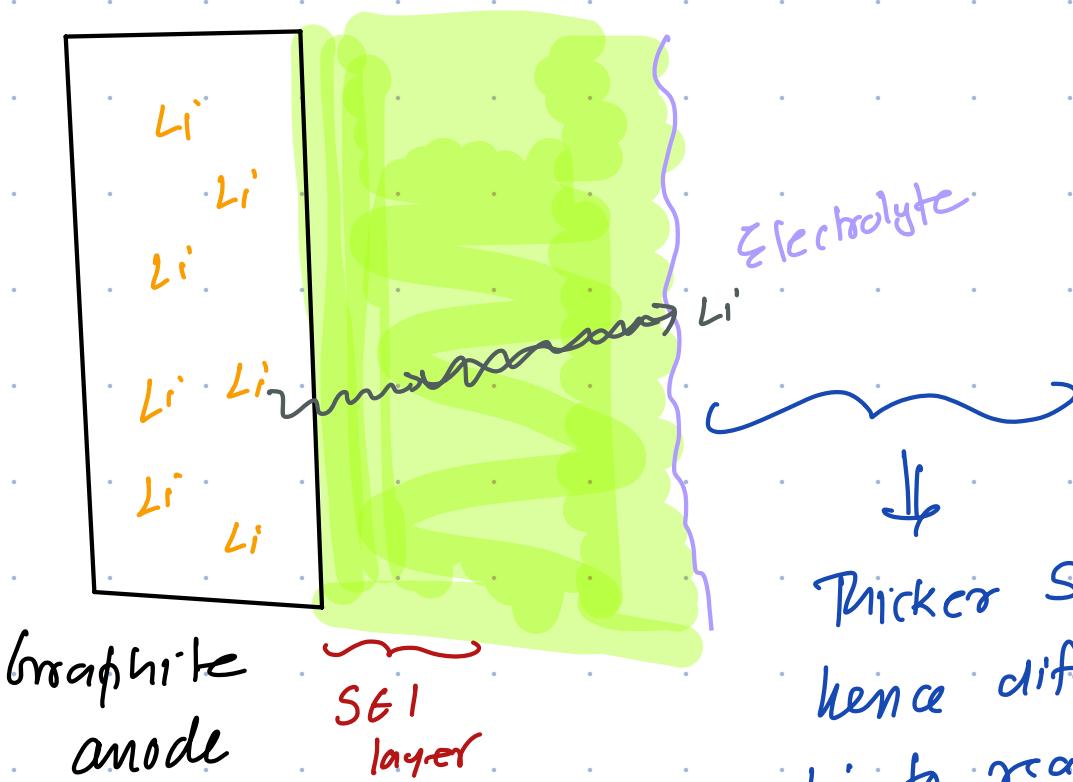
\Rightarrow SEI transformation = SEI layer thick

At $t = t_1$



* Li diffuses through
SEI layer and
reaction happens.

At $t = t_2$ where $t_2 > t_1$



Thicker SEI \Rightarrow
hence diffusion of
Li to reach electrolyte
faces resistance.



Thickness of SEI influence
rate of reaction

* Hence, instead of Arrhenius model, we choose
diffusion-type kinetic model which tells
(i) peak narrowing \rightarrow faster heating = less time for diffusion
↓
faster $\propto n$
(ii) low temp shift \rightarrow shifted Arrhenius plot

* Model

x_{Lic} = Dimensionless concn of lithiated graphite

t_{SEI} = thickness of SEI layer

Governing equations \times

(i) Rate of change of Lithiated graphite

$$\frac{dx_{\text{Lic}}}{dt} = \left[\text{Rate of prodn of Lithiated graphite} - \text{Rate of consumption of Lithiated graphite} \right]$$

$$\frac{dx_{\text{Lic}}}{dt} = -A_{\text{Lic}} x_{\text{Lic}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI}, \text{ref}}}\right)$$

where k = Boltzmann constant
 $(1.38 \times 10^{-23} \text{ J/K})$

(ii) Rate of change of SEI thickness

$$\frac{dt_{\text{SEI}}}{dt} = A_{\text{Lic}} x_{\text{Lic}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI}, \text{ref}}}\right)$$

(iii) Heat release

$$Q = -\Delta H_{\text{LiC}} \cdot \frac{dx_{\text{LiC}}}{dt}$$

Assumptions

- * Formation of S-SEI is rate determining step
- * Overall kinetics in region 2 determined by S-SEI formation
- * First order rxn; no nonlinear temp dependence
- * of rate constant

Challenges

- * Initial condition for SEI thickness $t_{\text{SEI}}(t=0)$
- * Modification of existing CRNN framework
- * RHS of the two ODE's are same; any smarter way to solve them / include in network.

Approach

→ Begin simple model

$$\frac{dx_{\text{LiC}}}{dt} = -A_{\text{LiC}} x_{\text{LiC}} \exp\left(\frac{-E_{\text{LiC}}}{kT}\right)$$

↔ One layer complexity → Non linearity

$$\frac{dx_{\text{Lic}}}{dt} = -A_{\text{Lic}} x_{\text{Lic}}^{\text{n}_{\text{Lic}}} T^{\text{b}_{\text{Lic}}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right)$$

↔ Diffusion type kinetic coupled ODE

$$\frac{dx_{\text{Lic}}}{dt} = -A_{\text{Lic}} x_{\text{Lic}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI, ref}}}\right)$$

$$\frac{dt_{\text{SEI}}}{dt} = A_{\text{Lic}} x_{\text{Lic}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI, ref}}}\right)$$

↔ Non-linear diffusion type coupled ODE

$$\frac{dx_{\text{Lic}}}{dt} = -A_{\text{Lic}} x_{\text{Lic}}^{\text{n}_{\text{Lic}}} T^{\text{b}_{\text{Lic}}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI, ref}}}\right)$$

$$\frac{dt_{\text{SEI}}}{dt} = A_{\text{Lic}} x_{\text{Lic}}^{\text{n}_{\text{Lic}}} T^{\text{b}_{\text{Lic}}} \exp\left(\frac{-E_{\text{Lic}}}{kT}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI, ref}}}\right)$$

Region 3: $200 \text{ }^\circ\text{C} < T < 300 \text{ }^\circ\text{C}$

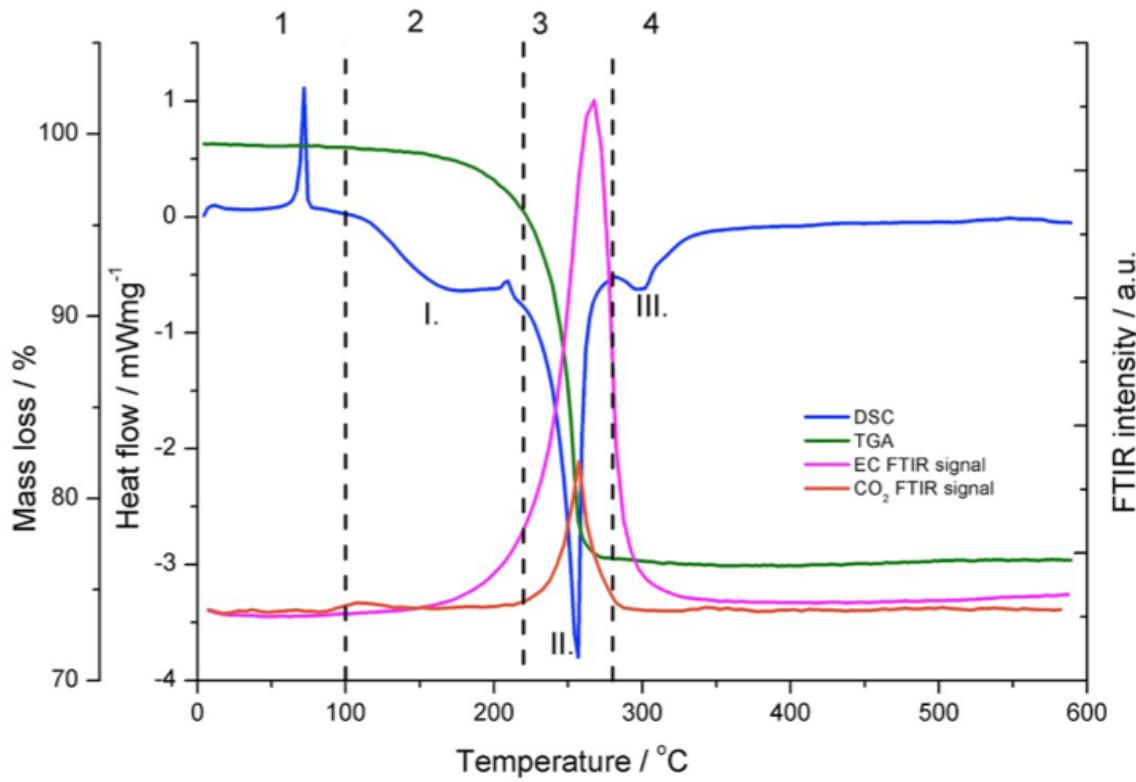
Region 2 $\Rightarrow 220 \text{ }^\circ\text{C} < T < 280 \text{ }^\circ\text{C}$

\Rightarrow Peak I \rightarrow (Exothermic)

\Rightarrow The region 2 exothermic heat comes from the following reactions

Jour

(a)

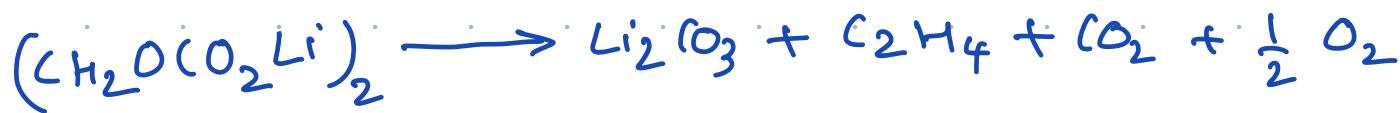


Key points

- * Much sharper & higher exothermic peak II
 Peak I in region 2 $\Rightarrow -0.8 \text{ mW/mg}$
 Peak II in region 3 $\Rightarrow -3.8 \text{ mW/mg}$
- * High mass loss + FTIR/GC shows significant gas evolution

POSSIBLE REACTIONS

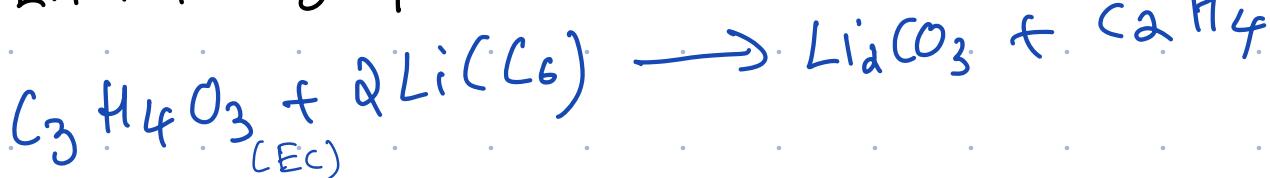
(1) SEI decomposition with gas evolution



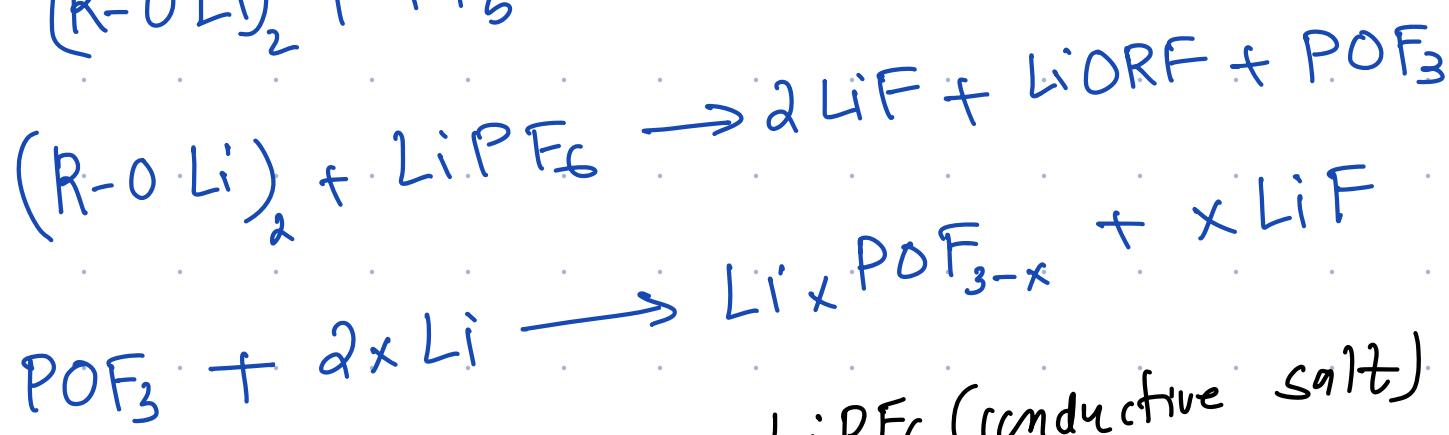
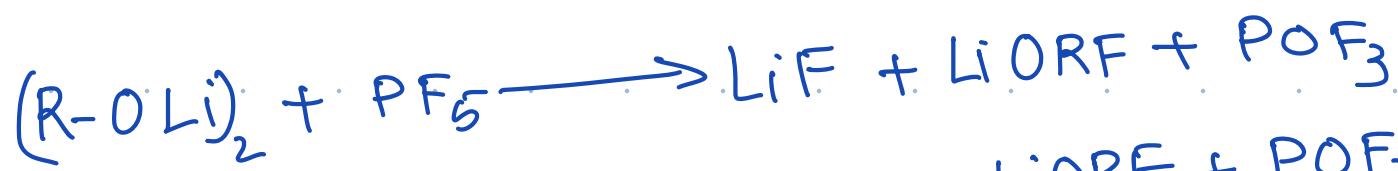
(2) SEI decomposition with Lithium



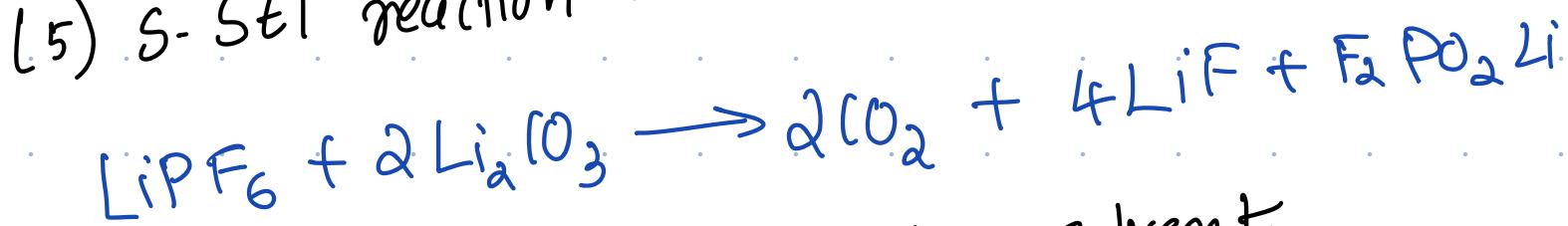
(3) Lithiated graphite reaction with electrolyte



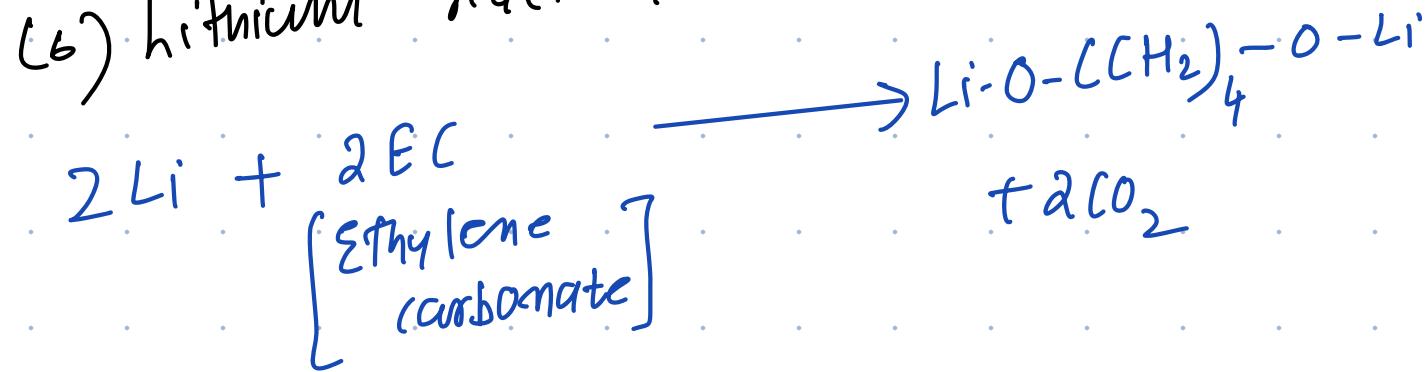
(4) S-STI reaction with conductive salt LiPF_6 in electrolyte



S-STI reaction with LiPF_6 (conductive salt)



Lithium reaction with EC solvent



Key points

x

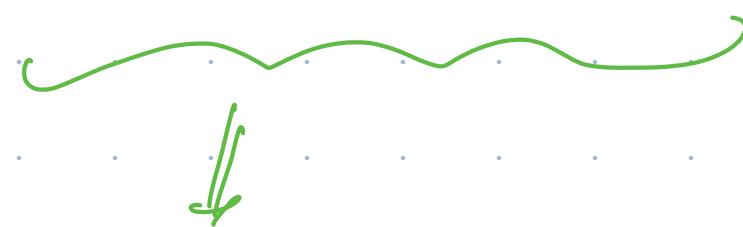
* FTIR | GC can detect $\rightarrow \text{CO}_2$ $\rightarrow \text{C}_2\text{H}_4$] \Rightarrow (1), (2) oxns ✓

$\rightarrow \text{PF}_3$] \Rightarrow reaction involving
 LiPF_6 ✓

* Ethylene carbonate decomposes in the range ($200 - 280^\circ\text{C}$), but we do not add these reactions here; because EC evaporates way before

* Reactions responsible for peak 2

→ Decomposition of SEI
→ Lithium reaction with electrolyte components
→ Decomposition of LiPF_6



The peak comes from superposition of multiple parallel reactions!



CRNN does support this!

* Slowest reaction \Rightarrow Most imp rxn for kinetics!

* Simplification methods

\rightarrow Single dominant reaction

\rightarrow Group rxns with similar reactants & products
into one effective reaction

* Proposed model

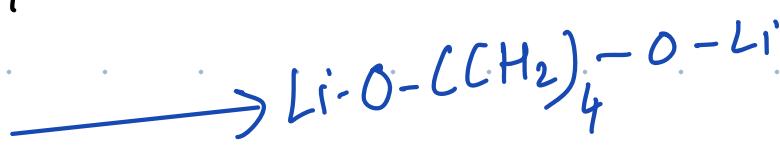
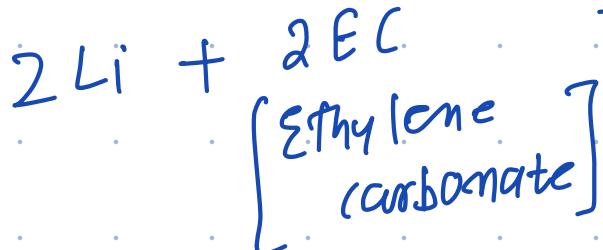
\rightarrow Most significant rxn are that involves solvent

$\xrightarrow{\text{EC}}$
 \rightarrow Rxn (3) & (6) considered

\rightarrow If slowest rxn follow Arrhenius, we
can model overall kinetics acca

Reactions for Peak 2

(1) lithium reaction with EC solvent



→ we see CO_2 in region 2 ✓

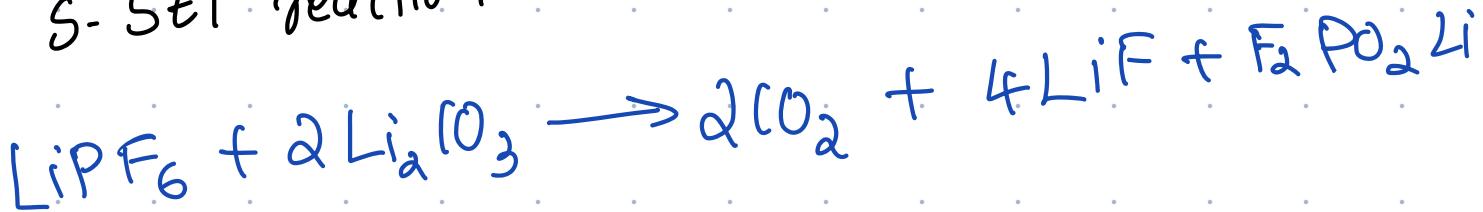
(2) SEI decomposition with Lithium



→ C_2H_4 is seen ✓

LiPF_6 (conductive salt)

(3) S-SEI reaction with



→ PF_3 detected

Kinetic model

X ————— X

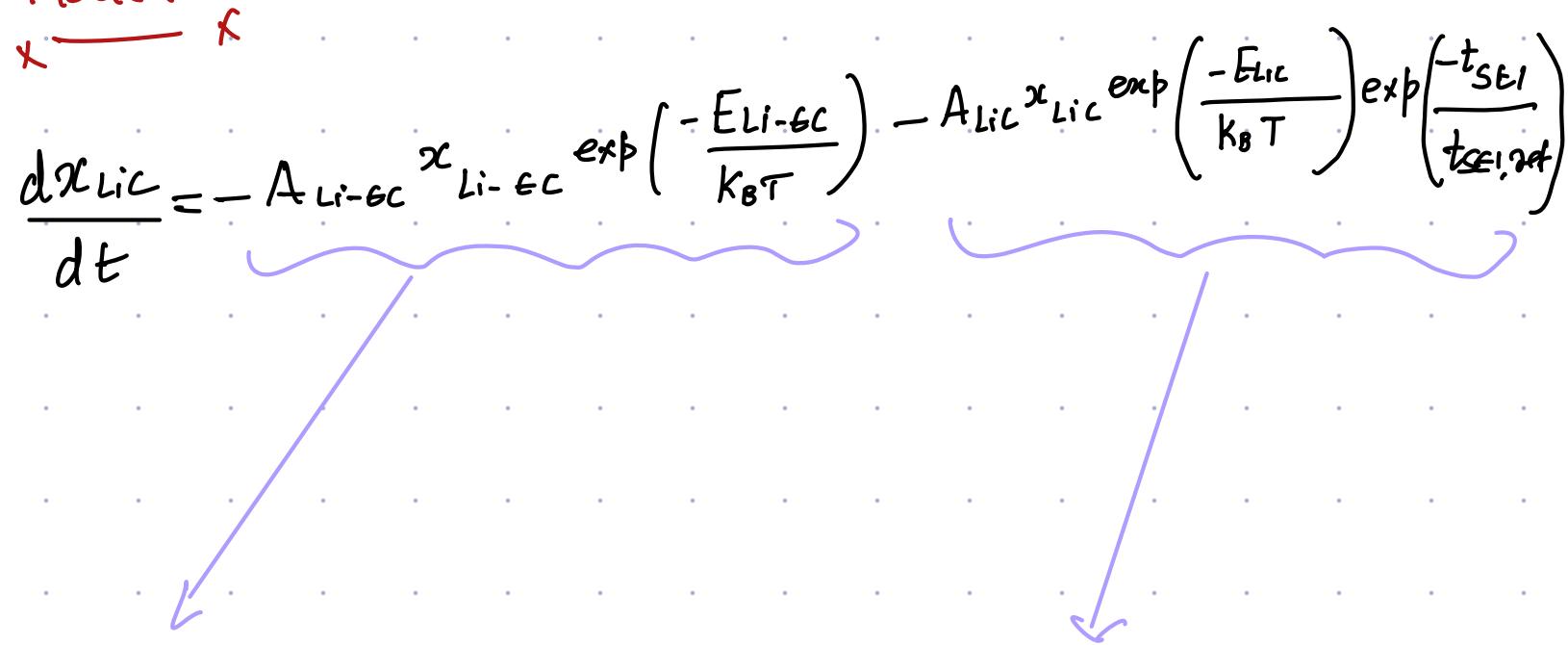
* Kinetic model in Region 3 is a modification
to the one in Region 2

↓

incorporates Li-EC & x_n & S-SEI decomposition
together

$$\frac{dx_{\text{LiC}}}{dt} = -A_{\text{Li-EC}} x_{\text{Li-EC}} \exp\left(-\frac{E_{\text{Li-EC}}}{k_B T}\right) - A_{\text{LiC}} x_{\text{LiC}} \exp\left(\frac{-E_{\text{LiC}}}{k_B T}\right) \exp\left(\frac{-t_{\text{SEI}}}{t_{\text{SEI},2d}}\right)$$

Model



Li-EC rxn

Arrhenius
model

Continuation of decimp.
of lithiated graphite
facilitated by the reduction
of SEI thickness.

Assumption

x — x

* EC is abundant \rightarrow Hence concn of EC not included in rate eqn

Actual \rightarrow

$$-A_{Li-EC} x_{Li-EC} EC \exp\left(-\frac{E_{Li-EC}}{k_B T}\right)$$

Assumption $\Rightarrow EC = \text{const}$ & hence incorporated into A_{Li-EC}

$$-A_{Li-EC} x_{Li-EC} \exp\left(-\frac{E_{Li-EC}}{k_B T}\right)$$

* Rate determining step \rightarrow formation & decomposition of S-SEI

So, $\frac{dx_{LiC}}{dt} = -g_{Li-EC} - g_i$

Thickness tsei reduce in region 3; So; we
see negative rate; [Not mentioned in paper]
TWO approaches $g_{SEI} = g_{LiC}$
(i) Assume $g_{SEI} = g_{LiC}$

$$\frac{dt_{SEI}}{dt} = -g_{SEI} = -g_{LiC}$$

$$= -A_{LiC} x_{LiC} T^{b_{LiC}} \exp\left(\frac{-E_{LiC}}{kT}\right) \exp\left(\frac{-t_{SEI}}{t_{SEI, ref}}\right)$$

(ii) Different model for SEI since two terms are involved \Rightarrow separate parameters.

$$\frac{dt_{SEI}}{dt} = - A_{SEI} \chi_{Lic}^{\eta_{Lic}} T^{\eta_{Lic}} \exp\left(\frac{-E_{SEI}}{k_B T}\right)$$

I think $t_{SEI}(t=0)$ in Reg:3 should be the final thickness $t_{SEI}(t=t_F)$ in the region

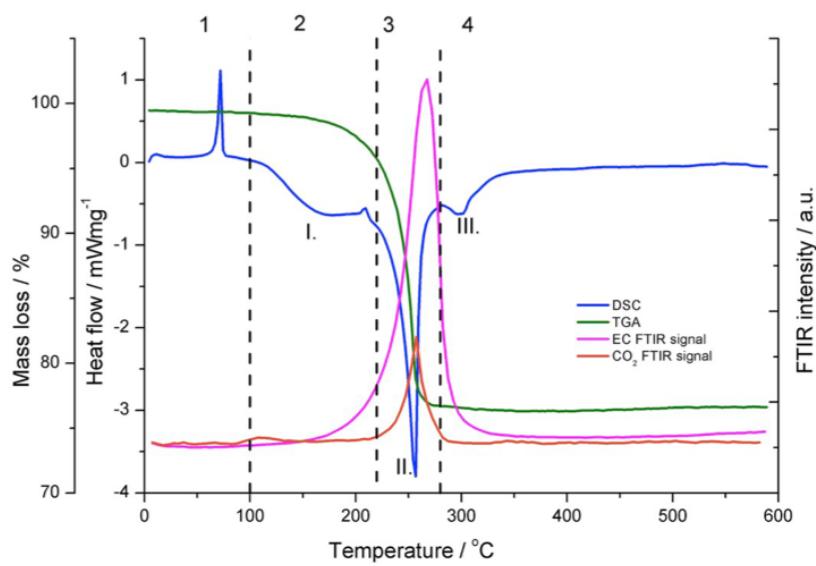
2!

NOTE

$\exp\left(\frac{-t_{SEI}}{t_{SEI}}\right)$ mean that as thickness \downarrow ; barrier decreases & rate \uparrow .



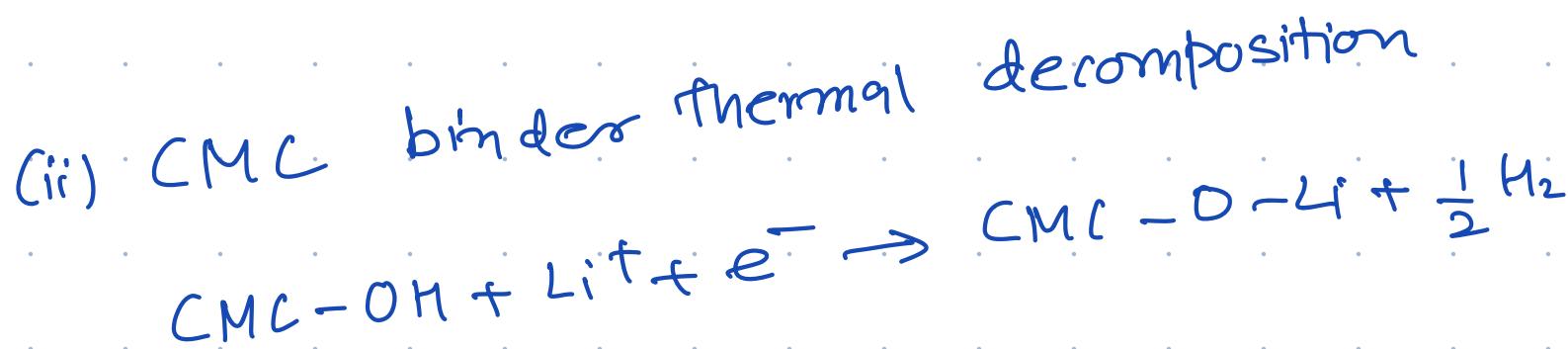
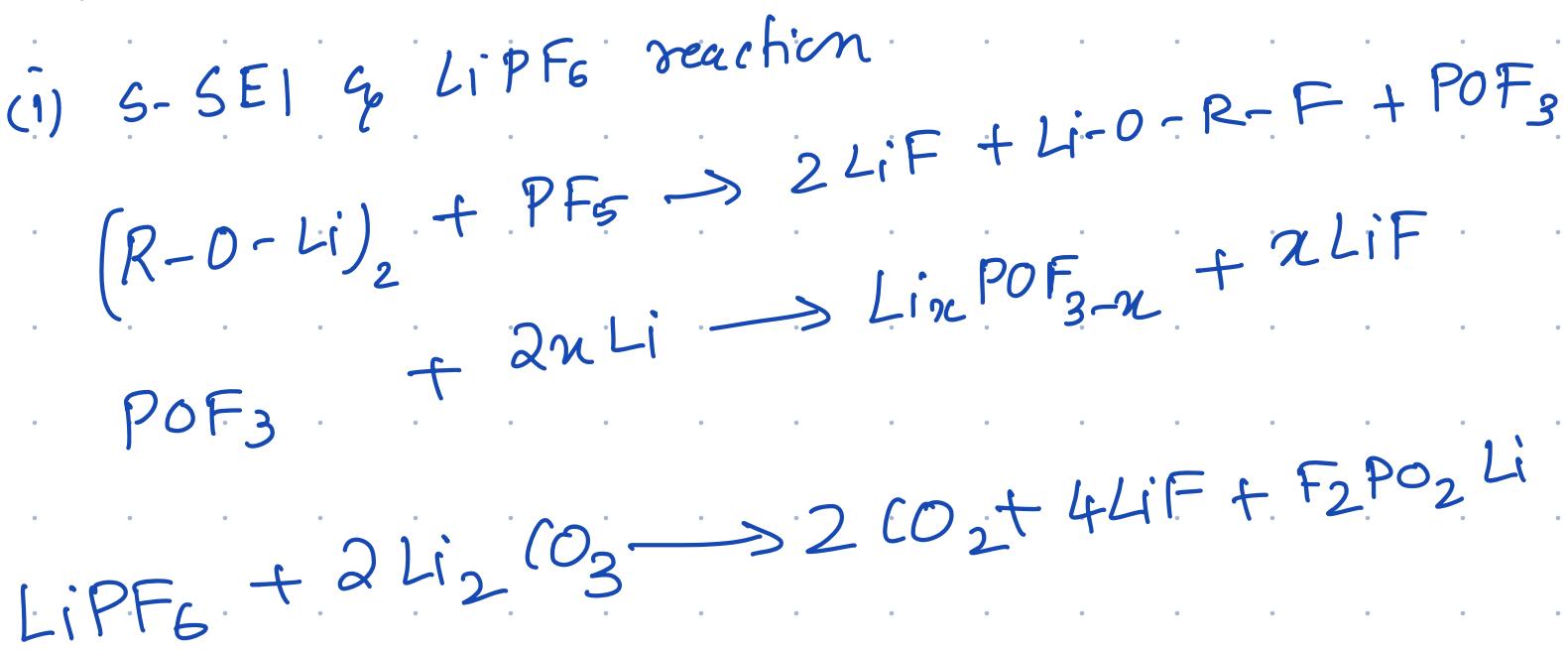
(a)



- * Smaller peak $\Rightarrow -0.5 \text{ mW/mg}$
- * less mass loss; detectable only @ 15 K/min heating
- * Multiple rxns involved

Potential reactions x

x



Proposed kinetic model

$$X \quad x$$

$$\frac{d\chi_B}{dt} = -A_B \chi_B \exp\left(\frac{-E_B}{k_B T}\right)$$

$\chi_B \Rightarrow$ dimensionless concn of binder & other
& products form previous reactions.