



МОНГОЛЫН ЭМЭГТЭЙ ИНЖЕНЕР ТЕХНОЛОГИЧ ЭРДЭМТЭН  
МАТЕМАТИКЧДЫН НЭГДСЭН ХОЛБООНЫ 5-Р ЧУУЛГА



**ENERGY**  
**NANO**  
UNIVERSITY OF ULSAN  
CHEMICAL ENGINEERING

# ЛИТИЙН ИОН БАТАРЕЙН АНОД ЭЛЕКТРОДОД ХЭРЭГЛЭГДЭХ ХОЛБОГЧ ПОЛИМЕР МАТЕРИАЛЫН СУДАЛГАА

**Supervisor:** Battsengel Baatar, Prof. Dr.rer.nat.  
Eun-Suok Oh, Ph.D.

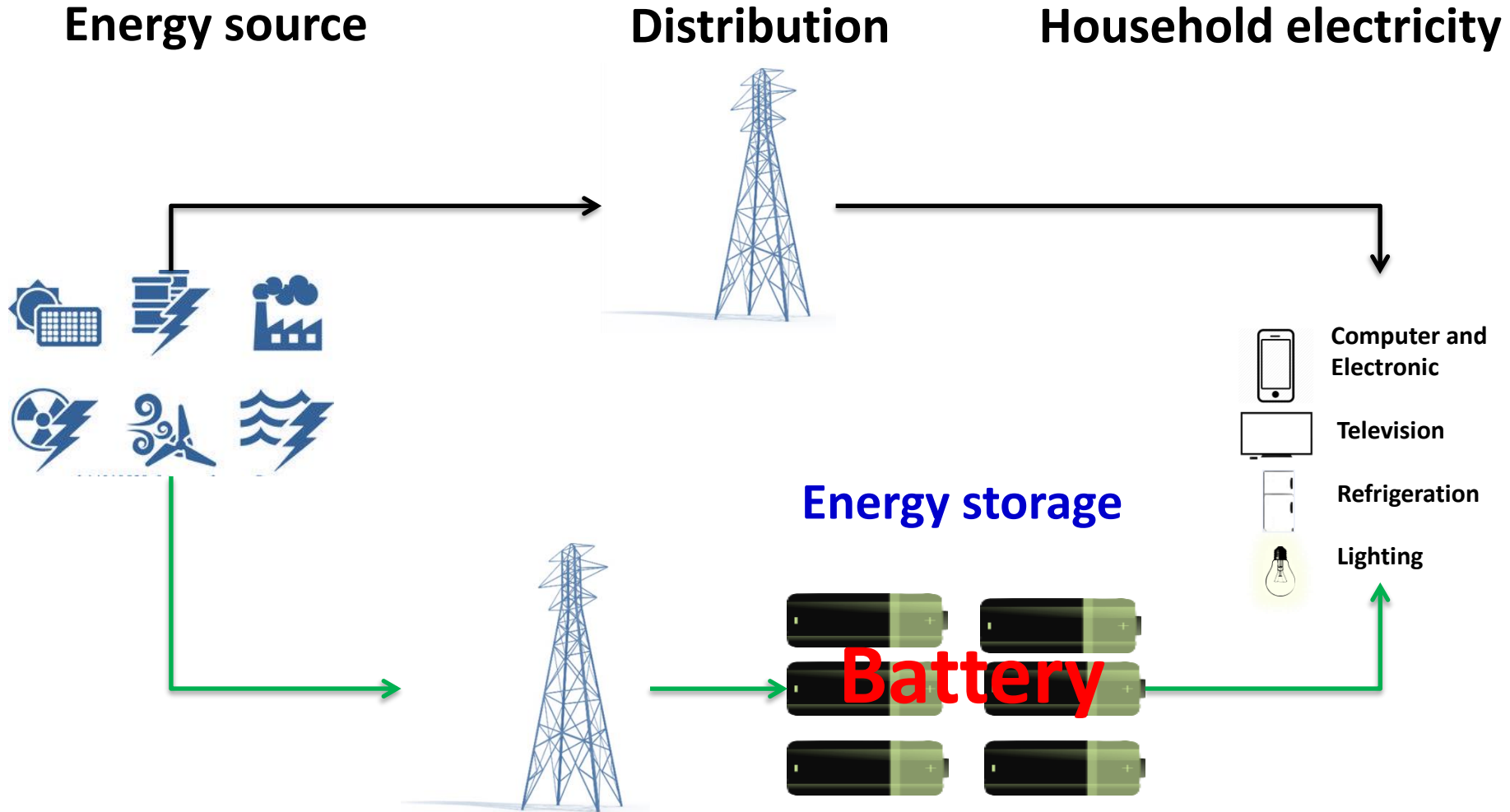
**Speaker:** Bolormaa Gendensuren Ph.D

Chem. Eng., Univ. of Ulsan

2020.10.31

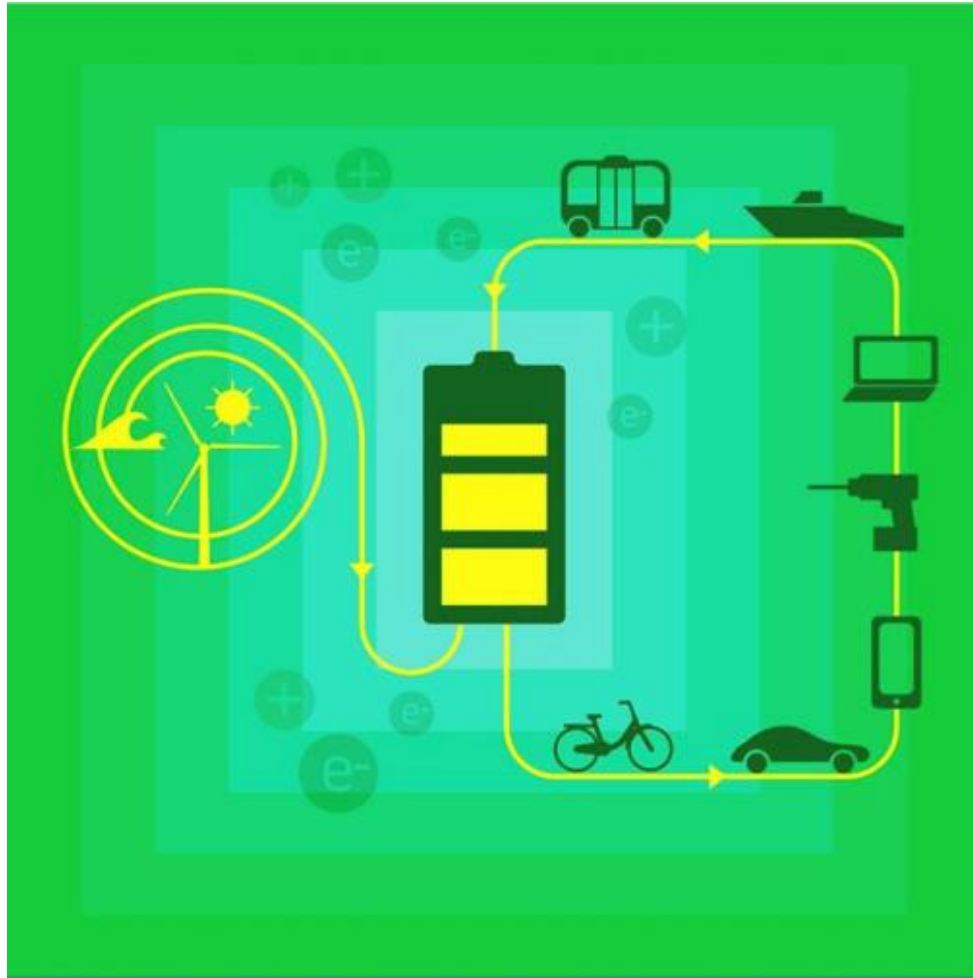
- ✓ **Introduction of polymer binder in LIB**
- ✓ **Dual-crosslinked Network binder for high-capacity Silicon based anode**

# Grid system & Energy storage



A smart grid system vs. reachable battery

# Lithium Ion Batteries (LIB)



## Advantage:

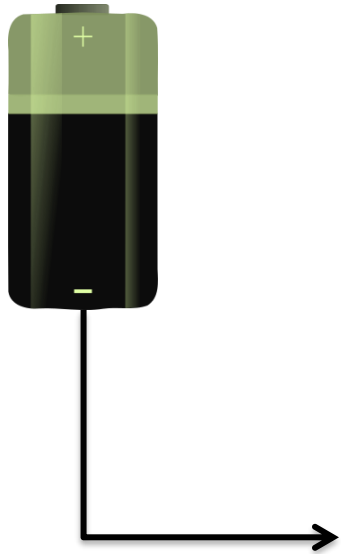
1. Various shape and size
2. No memory effect
3. Environment friendly
4. Low cost
5. High voltage
6. Large energy density
7. High cycle-life
8. Low self-discharge rate

## Kakao T bike

(LIB cell made by Samsung SDI Co.)

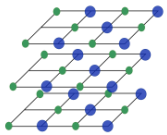


## Reversible electrochemical redox reaction



**Cathode material**

Layered oxide

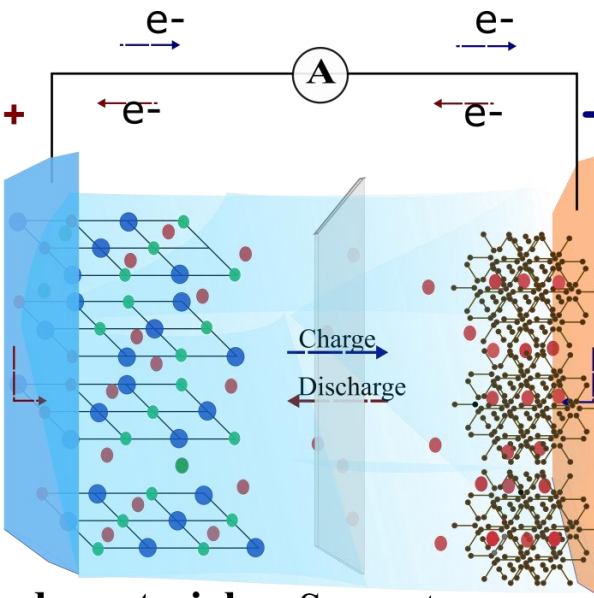


O3-type    P2-type

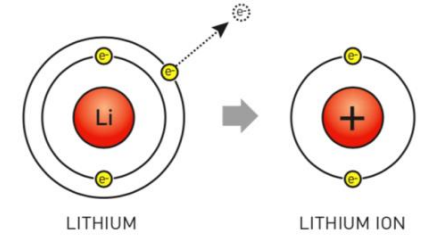
**Cathode materials:**    **Separator**    **Anode materials:**

LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub> etc.

Graphite, LTO, Si, Sn, etc.



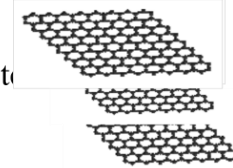
1	H		
3	Li	4	Be
11	Na	12	Mg
19	K	20	Ca
37	Rb	38	Sr
		21	Sc
		39	Y



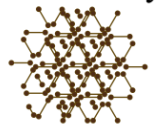
© Johan Jarnestad/The Royal Swedish Academy of Sciences

**Anode material**

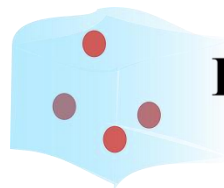
Carbonaceous



Metal alloy



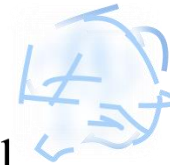
Metal oxide



**Electrolyte**

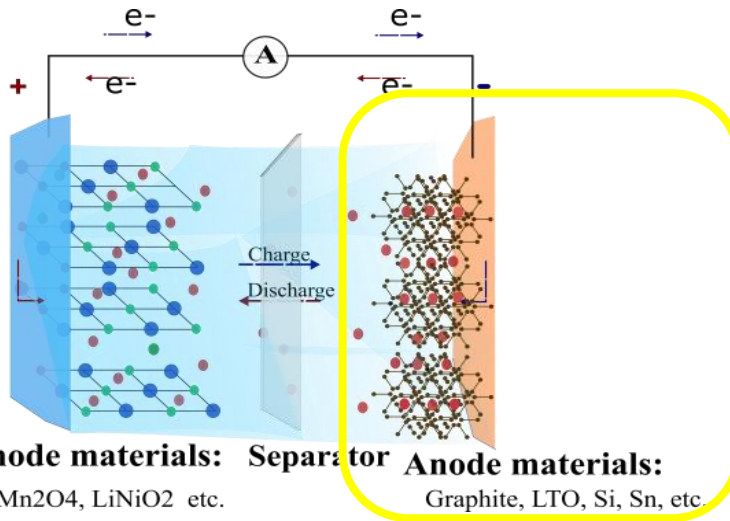


**Conductive material**

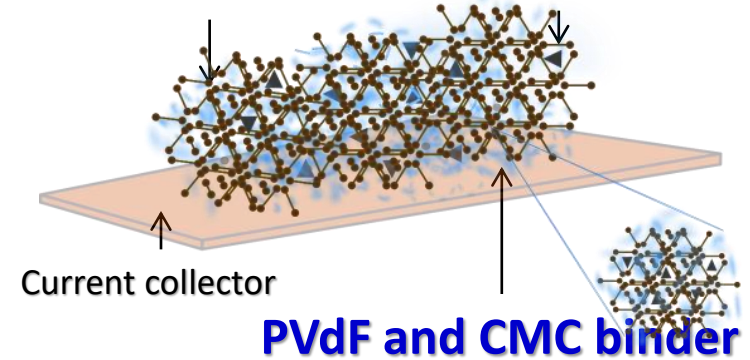


**Binder**

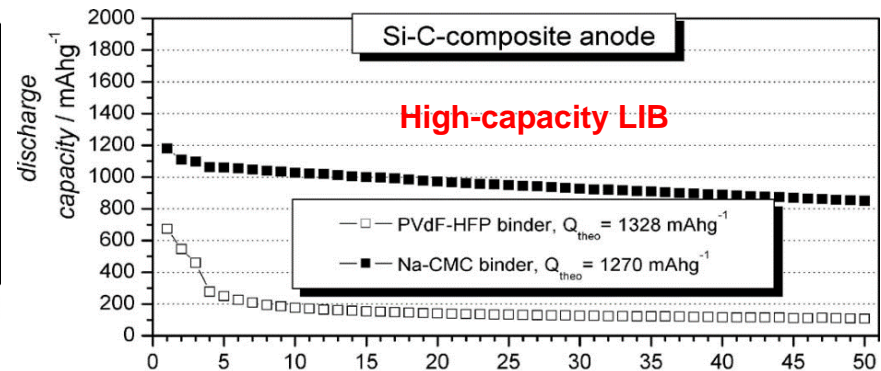
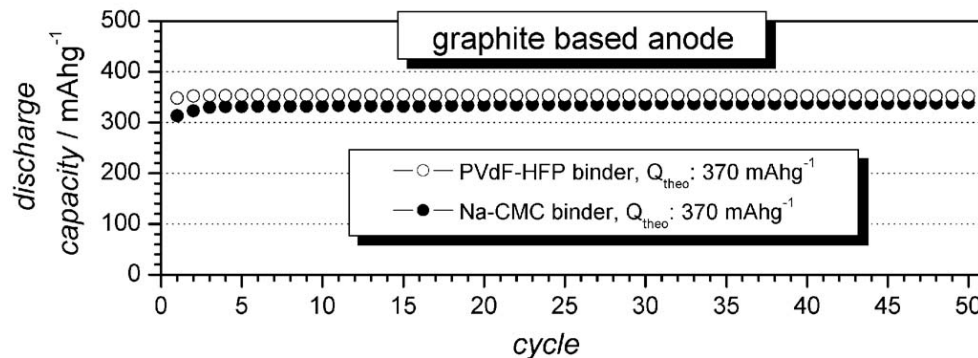
# Influence of Binder Chemistry

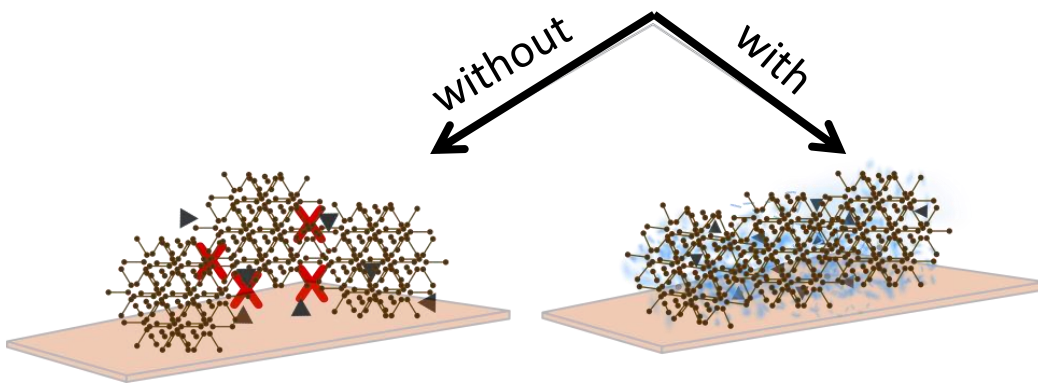


**vs. Anode Material** Conductive material



Hochgatterer et al., *Electrochem. Solid-state Lett.* 11, A76 (2008)





- The **binder** is used to **glue** active materials and conductive agent **together** with the current collector.
- 2-5 wt% for LIB
- Electrochemical inactivity

## Battery Binder Criteria:

### ➤ Adhesion strength

- Between AM
- Between AM and current collector

### ➤ Stability

- Chemical
- Electrochemical
- Thermal

### ➤ Processability

- Binder solution
- Electrode paste

### ➤ Mechanical strength

- Tensile strength
- Elongation

### ➤ **Electronic/Ionic conductivity**

# Polymer binder for high-cap. Si/C anodes

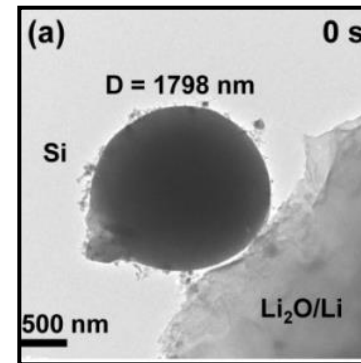
- **Dual-Crosslinked Network Binder**



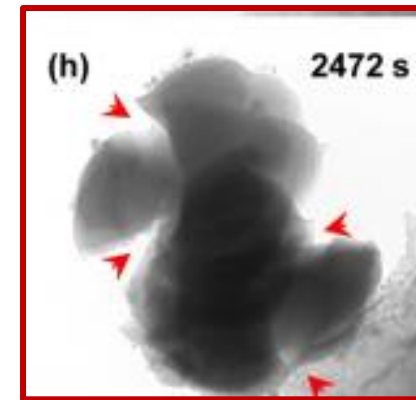
	Graphite	Silicon (High-capacity)	Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> (High-power)
Redox reaction	$C_6 + Li^+ + e^- \leftrightarrow LiC_6$	$Si + 4.4Li^+ + 4.4e^- \leftrightarrow Li_{4.4}Si$	$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \leftrightarrow Li_7Ti_5O_{12}$
Capacity	372 mAh g <sup>-1</sup>	4200 mAh g <sup>-1</sup>	175 mAh g <sup>-1</sup>
Characteristics	<ul style="list-style-type: none"> <li>✓ Volume change ~10 %</li> <li>✓ High reversibility &amp; stable capacity</li> </ul>	<ul style="list-style-type: none"> <li>✓ <b>High capacity</b></li> </ul>	<ul style="list-style-type: none"> <li>✓ no structural change (zero-strain)</li> <li>✓ High insertion potential ~1.55 V</li> </ul>
Drawbacks	<ul style="list-style-type: none"> <li>✓ Low capacity</li> <li>✓ Safety issue for dendrite</li> </ul>	<ul style="list-style-type: none"> <li>✓ <b>Significant volume change ~ 310%</b></li> <li>✓ Pulverization &amp; electrical disconnection</li> <li>✓ Rapid capacity fade</li> </ul>	<ul style="list-style-type: none"> <li>✓ <b>Electronic insulator</b></li> <li>✓ <b>Poor ionic diffusion</b></li> <li>✓ High residual water</li> </ul>
Polymer Binder	PVdF, SBR/CMC (< 3 wt%)	No polymer available (> 10 wt%)	Not chosen (~5 wt%)
Research trend		<p><b>Adhesion</b></p>	<p><b>Ion/electron transport</b></p>

## Silicon :

- ✓ High capacity (4200 mAh/g)
- ✓ Significant volume change during charge/discharge (310%)

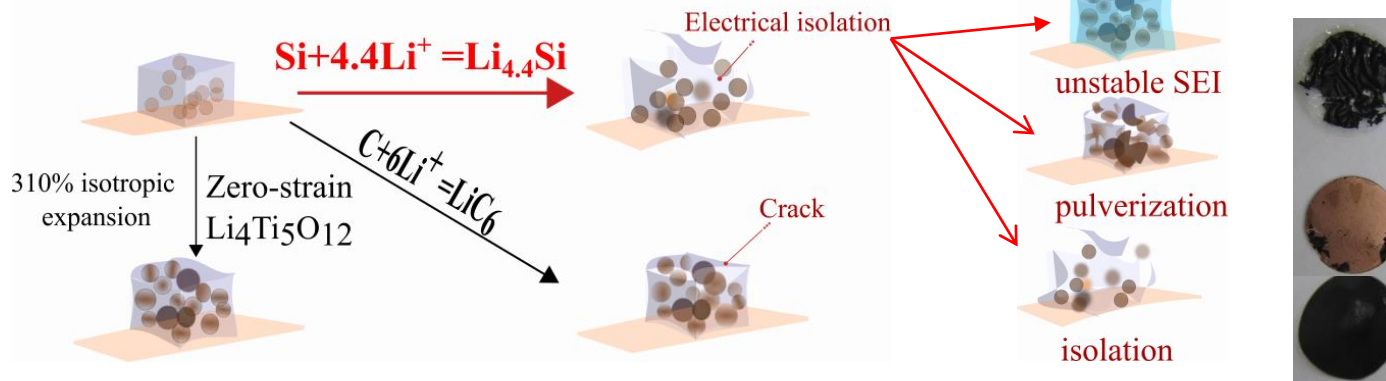


Liu et al., JACS Nano 6(2), 1522 (2012)



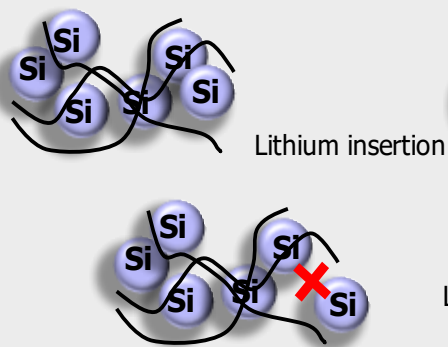
During lithium insersion

## Main Problem of Si

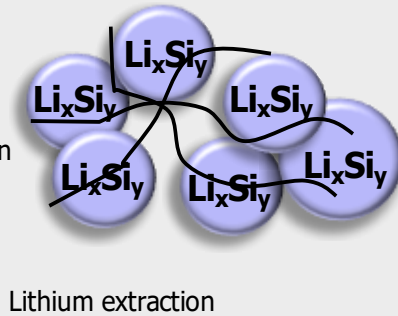


## Solution:

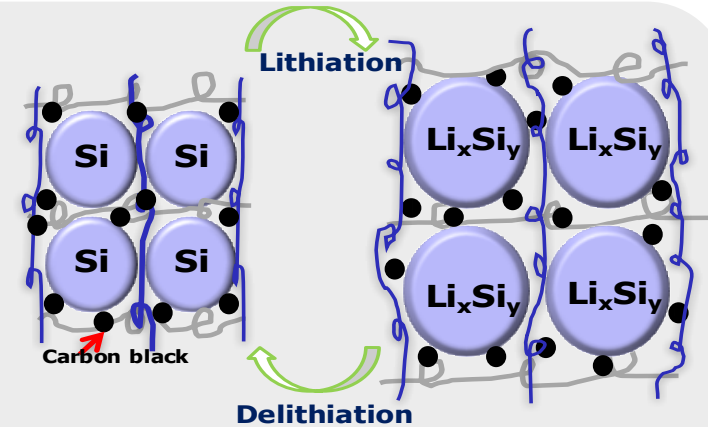
- Nanostructured design: Si NP, Si/C composite, Si alloy
- **New polymeric binder**



Conventional structure with linear chain polymers



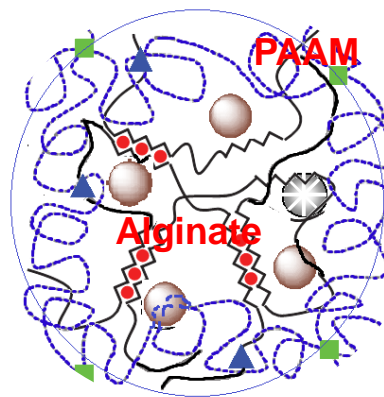
adhesion



Network structure with a dual-crosslinked polymer

## ❖ Dual-crosslinking between Alginate-Polyacrylamide

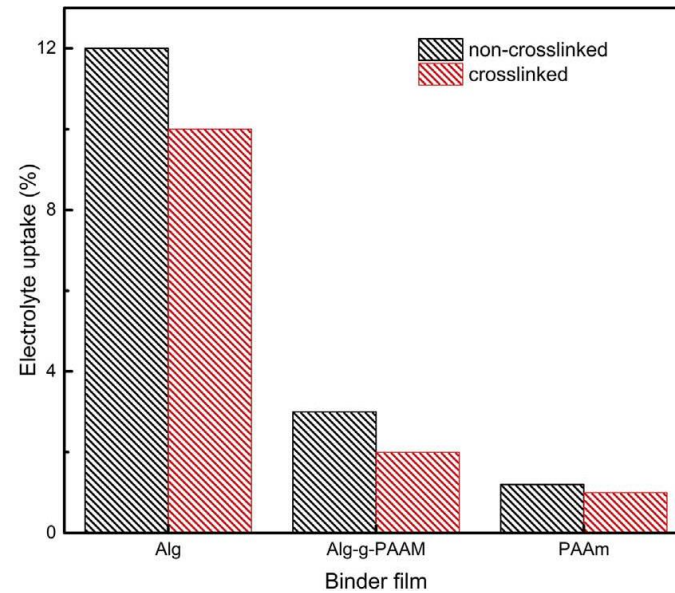
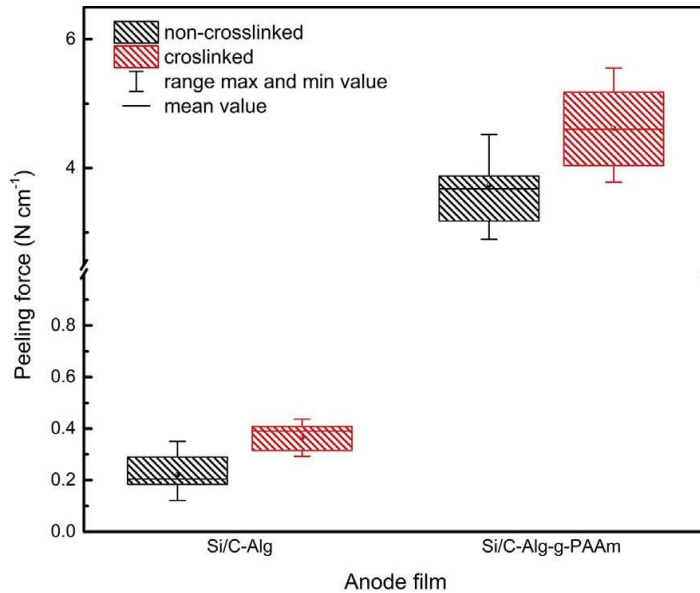
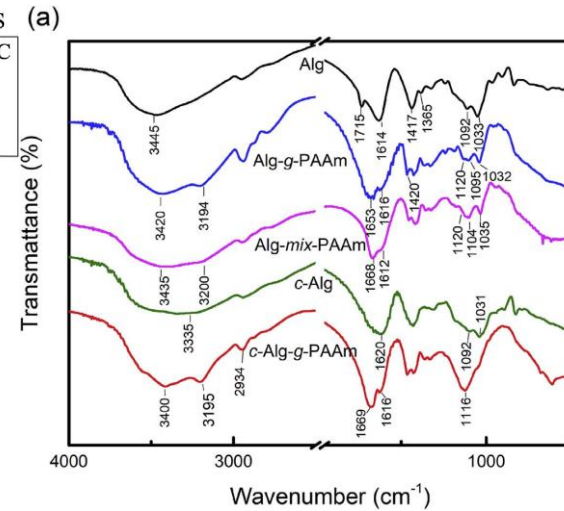
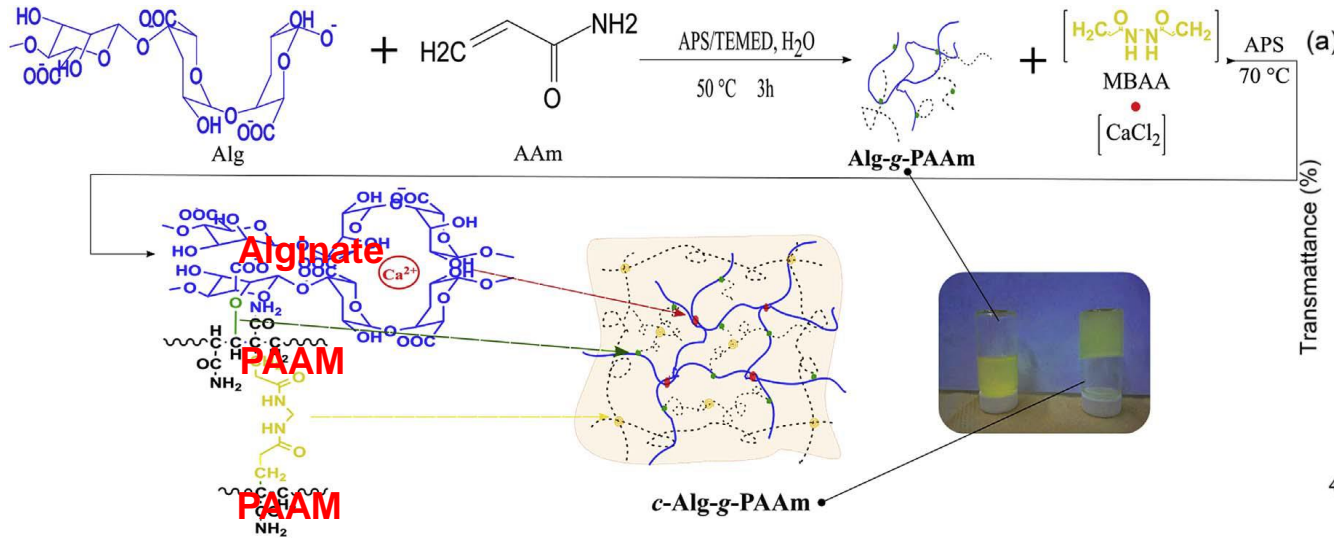
- ✓ Ionic (physical) crosslink: Alginate
- ✓ Chemical crosslink: Polyacrylamide



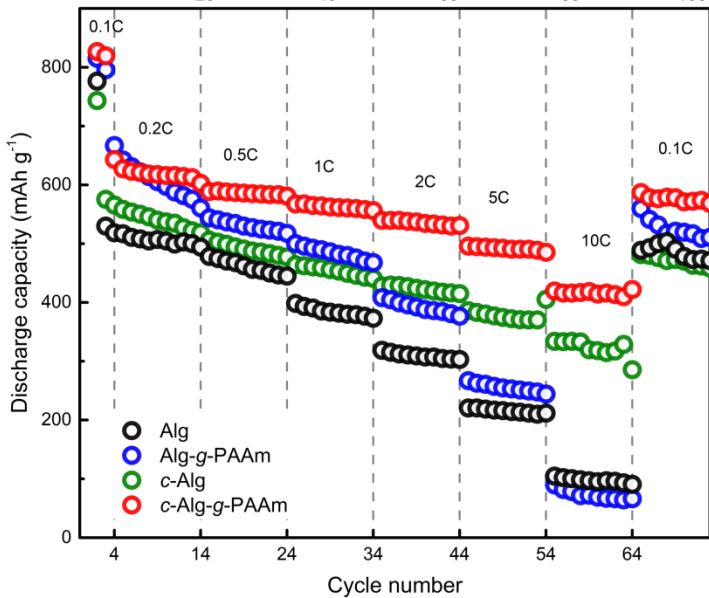
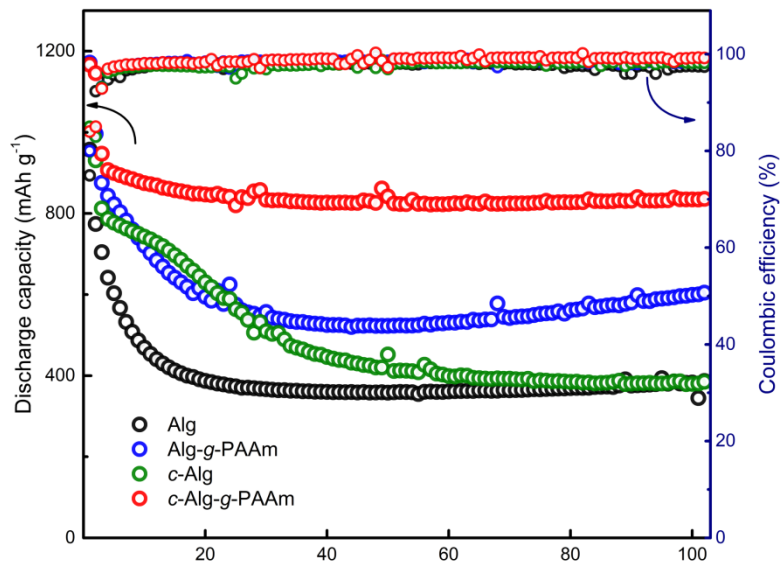
- Physical connected alginate with  $\text{Ca}^{2+}$  ions
- Covalent bond between alginate and PAAM
- Chemically crosslinked PAAM with MBAA
- Active materials such as Si particles
- Others such as graphite or Super P

B. Gendensuren and E.-S. Oh, *J. Power Sources* 384, 379 (2018)

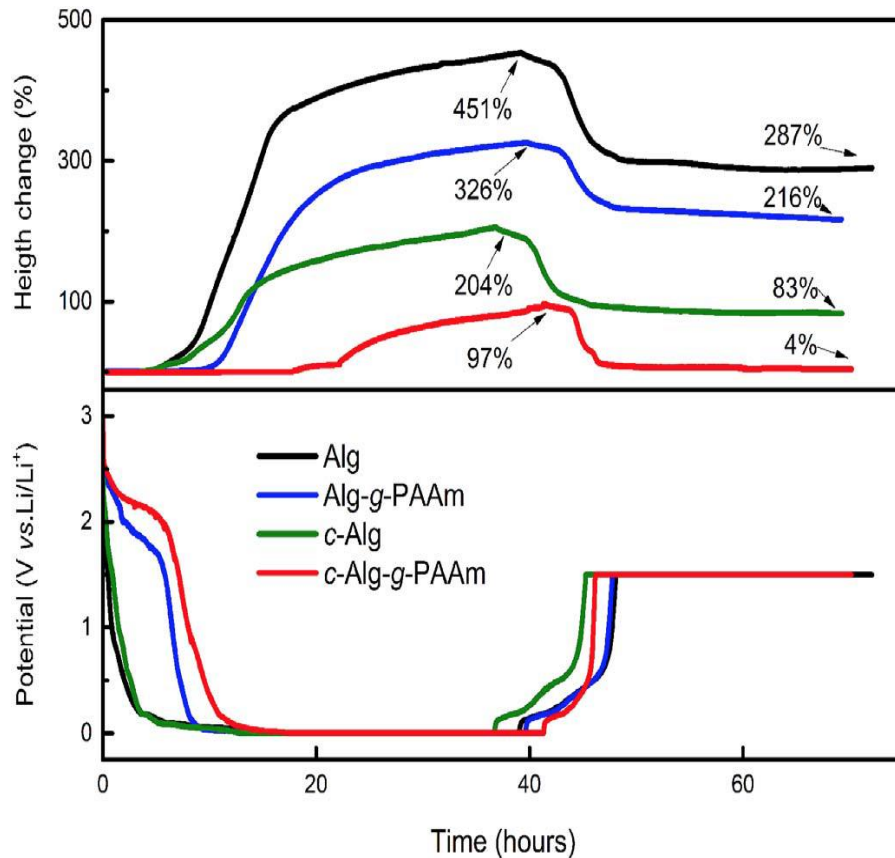
# Dual-crosslinked binder



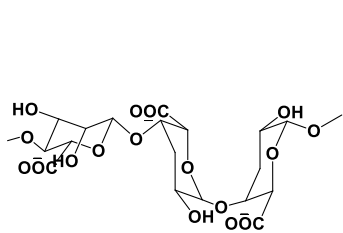
B. Gendasuren and E.-S. Oh, *J. Power Sources* 384, 379 (2018)



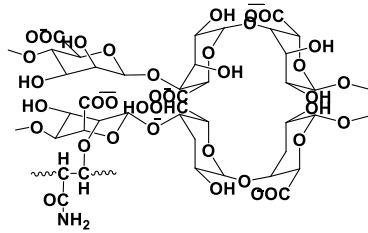
Theoretical volume expansion = 85% (Si:C=1:3)



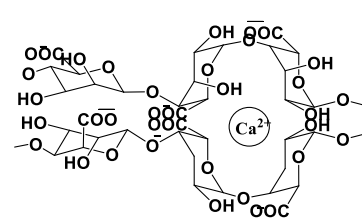
B. Gendensuren and E.-S. Oh, *J. Power Sources* 384, 379 (2018)



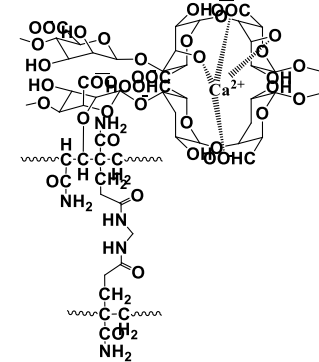
Alginate  
(Alg)



Alginate-g-Polyacrylamide  
(Alg-g-PAAm)



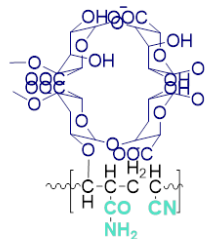
crosslinked Alginate  
(*c*-Alg)



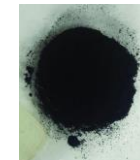
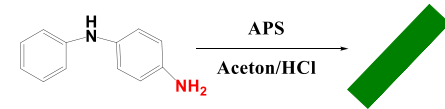
dual-crosslinked Alg-g-PAAm  
(*c*-Alg-g-PAAm)

- ✓ Successful synthesis of graft copolymer and establishment of dual-crosslinked network in linear alginate
- ✓ Enhanced adhesion with current collector
- ✓ Improving the electrochemical performance of Si/C anode with *c*-Alg-g-PAAm

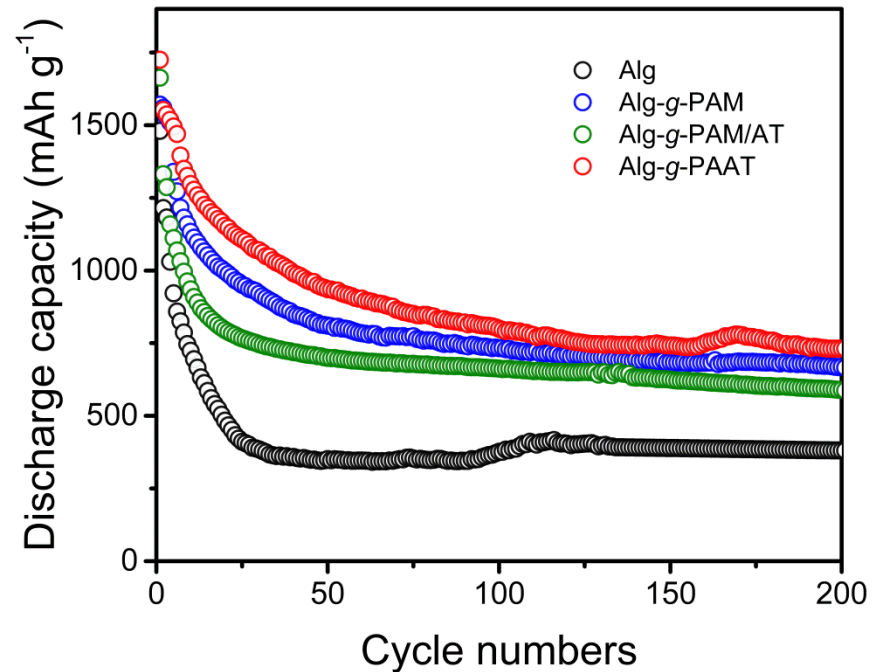
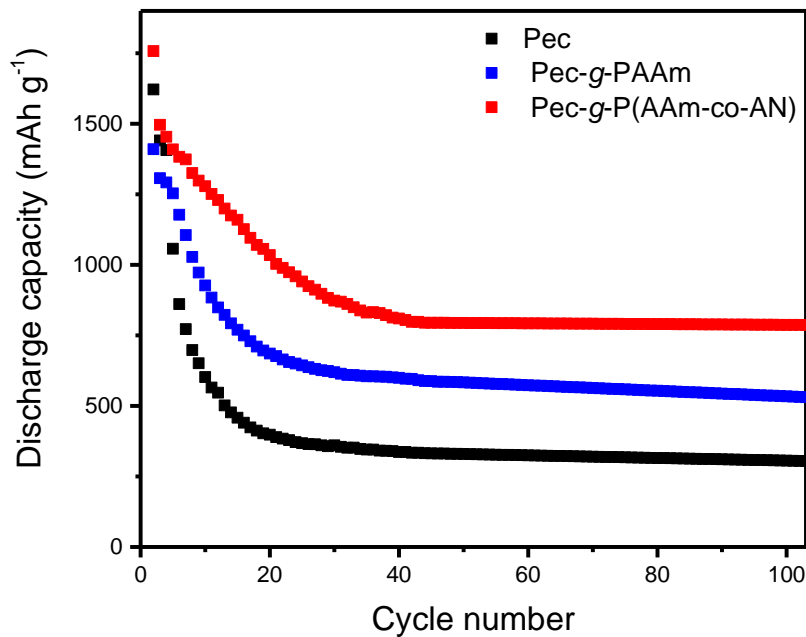
## ➤ Water-treated conductive self-healing polysaccharide based binders for high capacity anode



Pec-g-P(Am-co-AN)



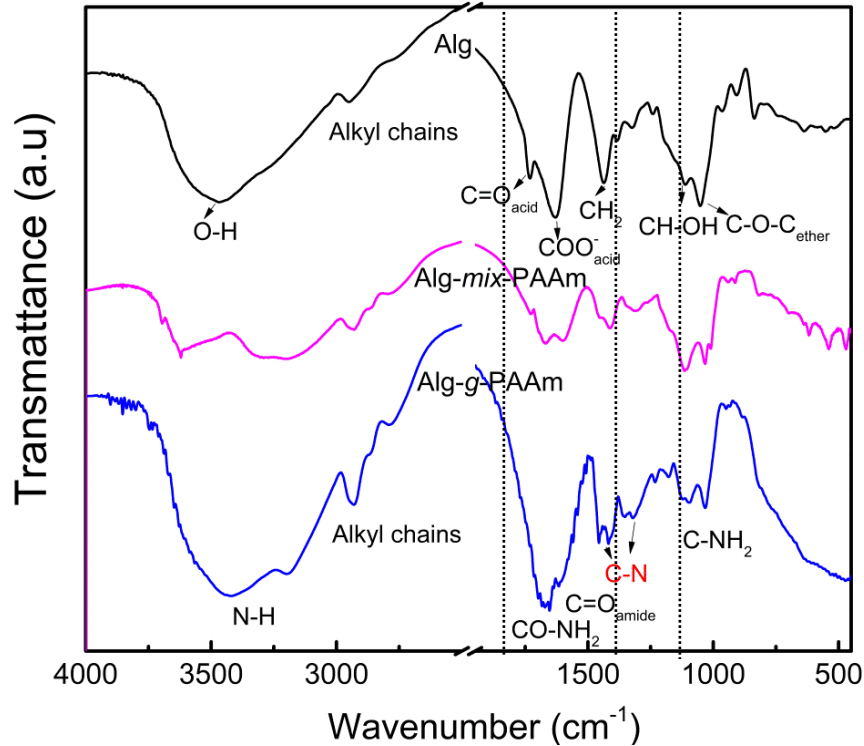
Aniline tetramer



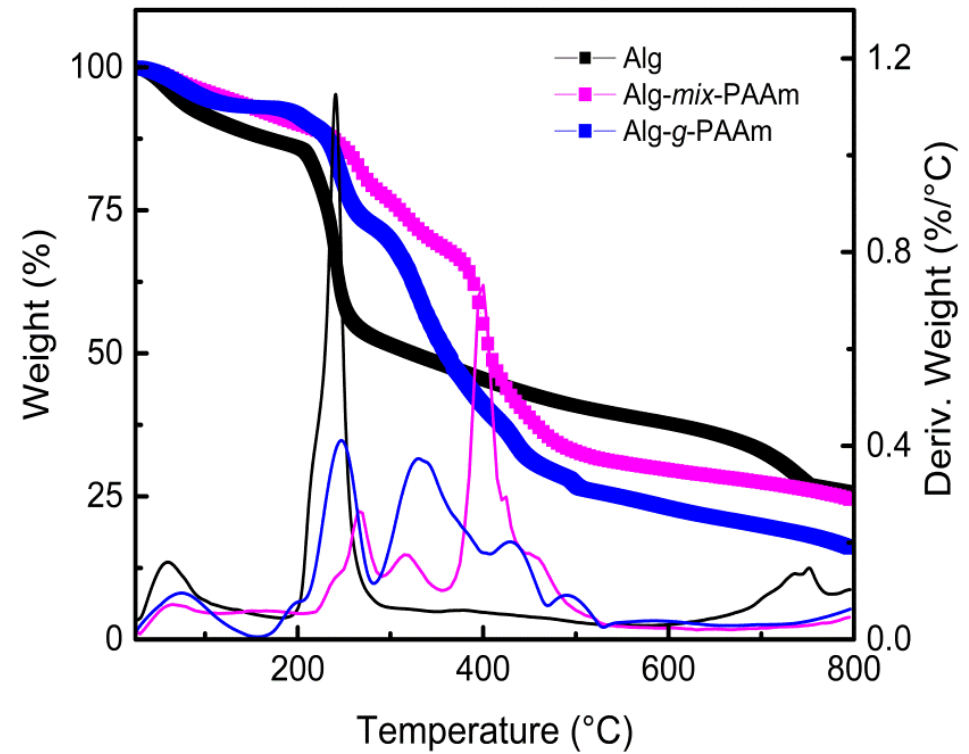
**THANK YOU FOR YOUR  
ATTENTION**



## FT-IR spectra

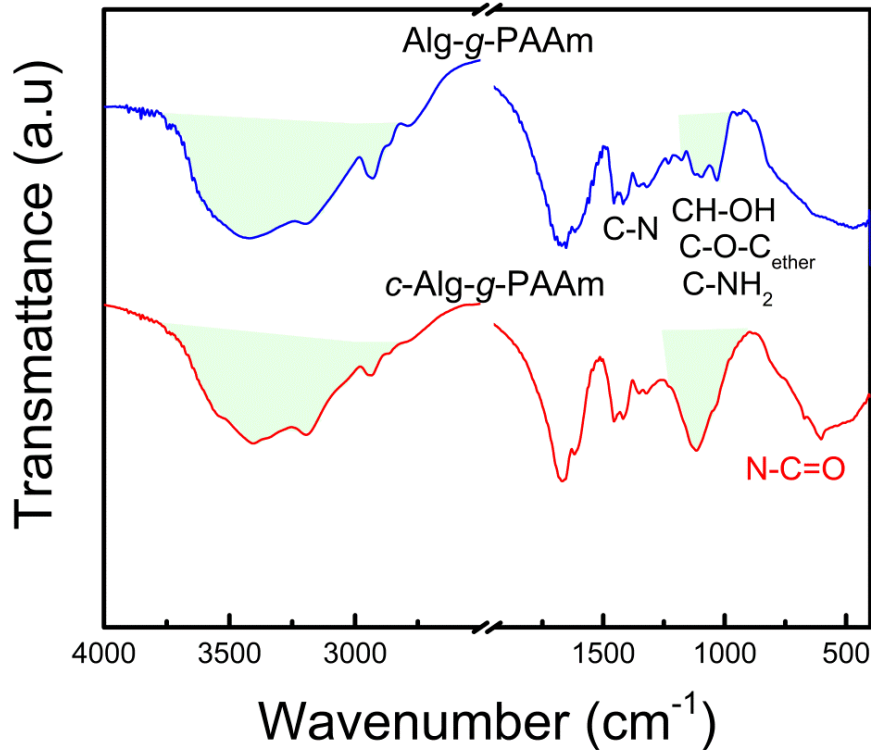


## TGA curve

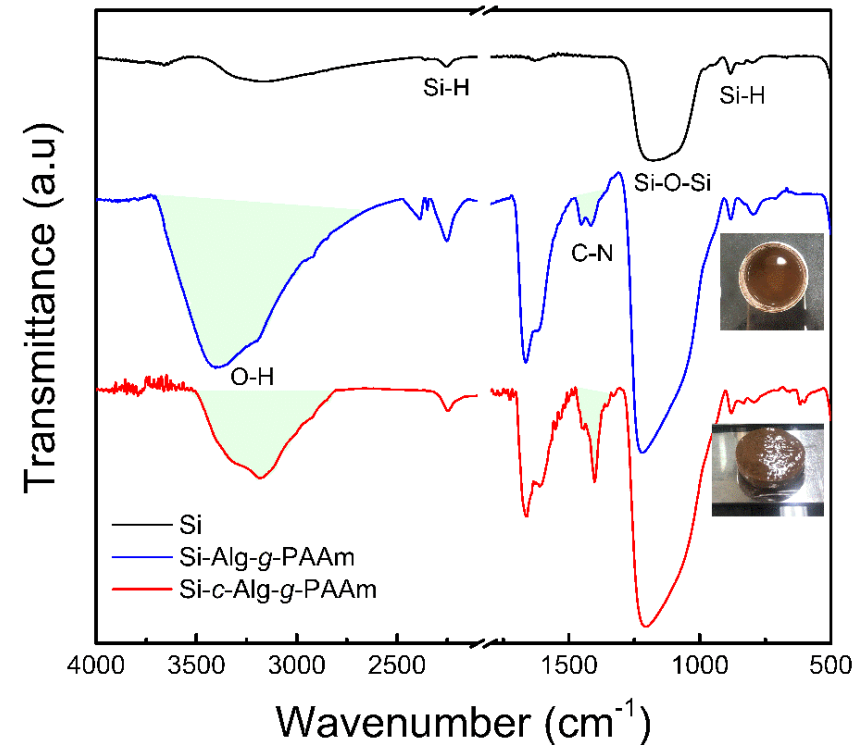


✓ **Successful grafting of PAAm onto alginate**

## FT-IR spectra of network



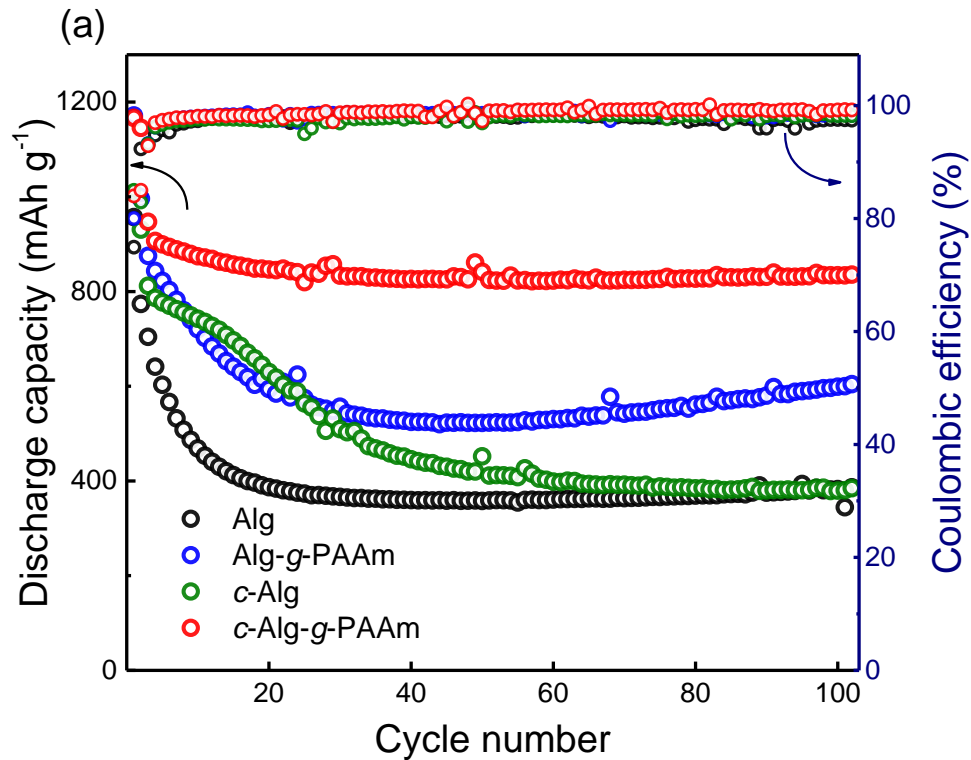
## FT-IR spectra of slurry



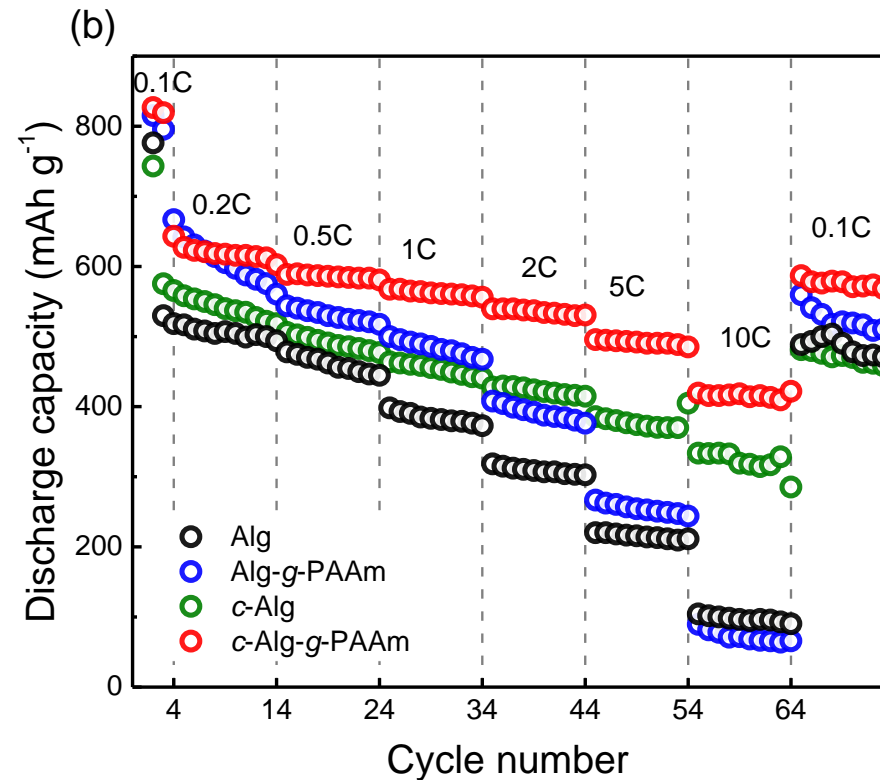
✓ **Achievement of dual-crosslinking in binder**

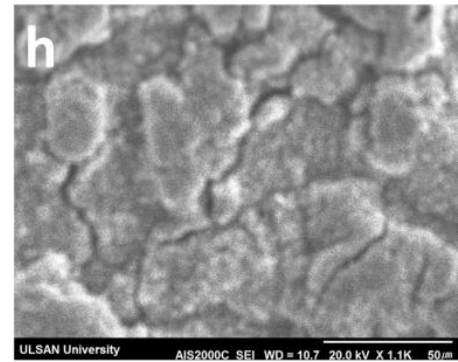
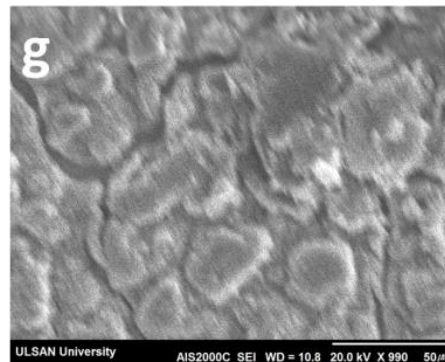
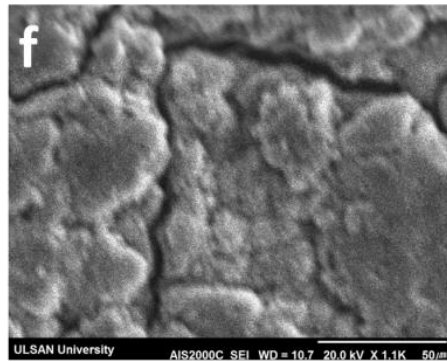
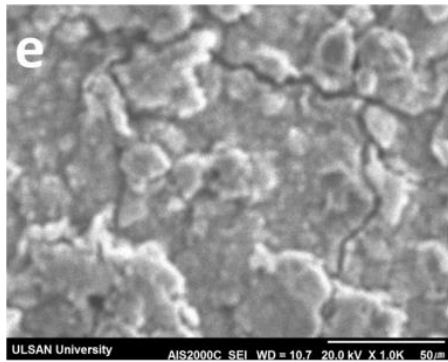
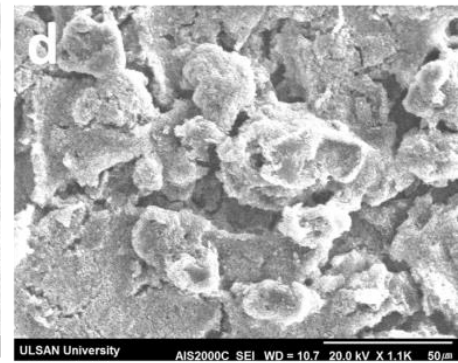
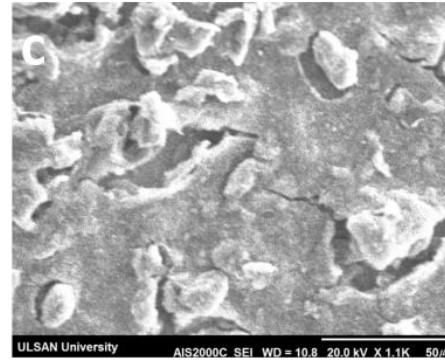
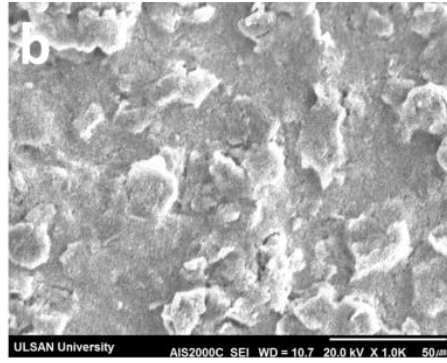
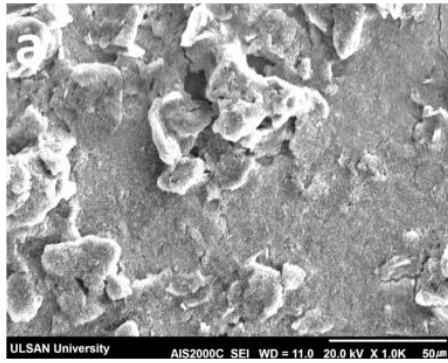
# Galvanostatic charge-discharge test

## Cyclic performance



## Rate capability test





Low magnification SEM images of Si/C electrodes with Alg (a and e), Alg-g-PAAm (b and f), c-Alg (c and g), and c-Alg-g-PAAm (d and h) before and after 100 cycles, respectively