

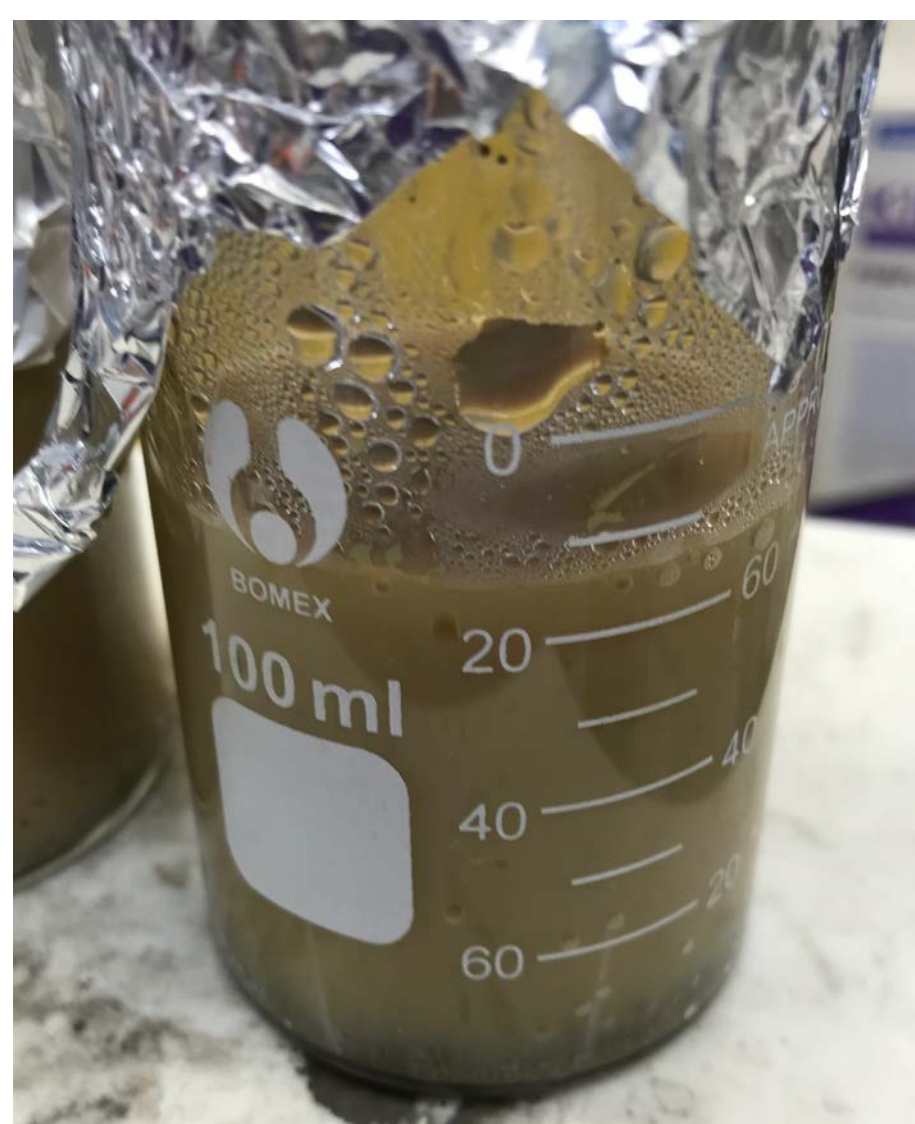
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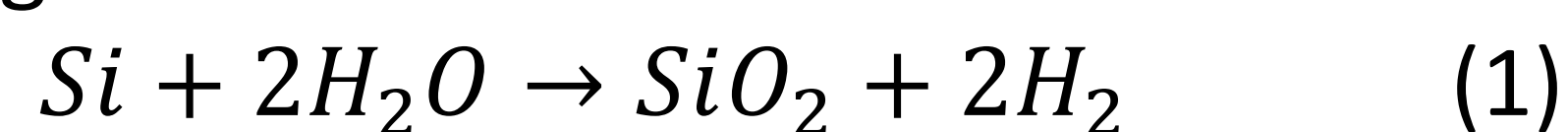
Introduction

The gravimetric capacity of carbon black anode applied in traditional lithium-ion batteries (LIB) is electrochemically limited to 372 mAh/g, which is deficient to power the ever-growing demands for portable electronic devices that require high energy density^[1]. Deemed as a potential game changer, Si nanoparticles (SiNPs) with a diameter less than 150 nm not only possess higher gravimetric capacity, but also experience least extent of fracturing during cycling^[2]. However, the large specific surface area tremendously increases Si oxides content, which are subjected to irreversible reactions with lithium, leading to low initial Coulombic efficiency. This project looks into mechanisms of Si oxides formation and their impacts on LIB performance, which shed light on methods of prolonging LIB lifetime.

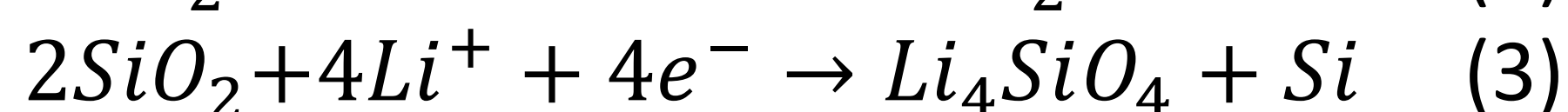
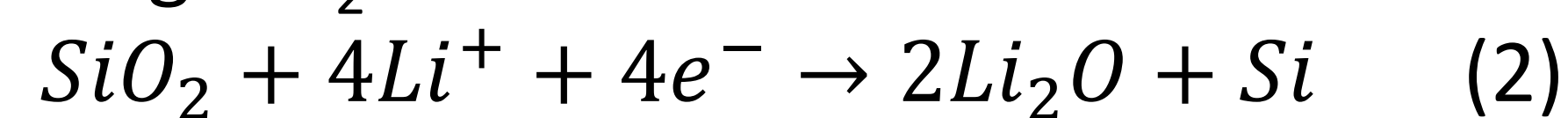
Si Wet Oxidation



Na-CMC is used as the binder, which requires water as the solvent. SiNPs oxidise in water according to ^[3]:



Resulting SiO₂ reacts with Li⁺ via ^[4]:



Both nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) show

the formation of Li₂O is reversible to some extent, but Li₄SiO₄ is not. Therefore, it is clear that the native oxide layer is playing a significant role in terms of electrochemistry, which is believed to be responsible for poor LIB cyclability.

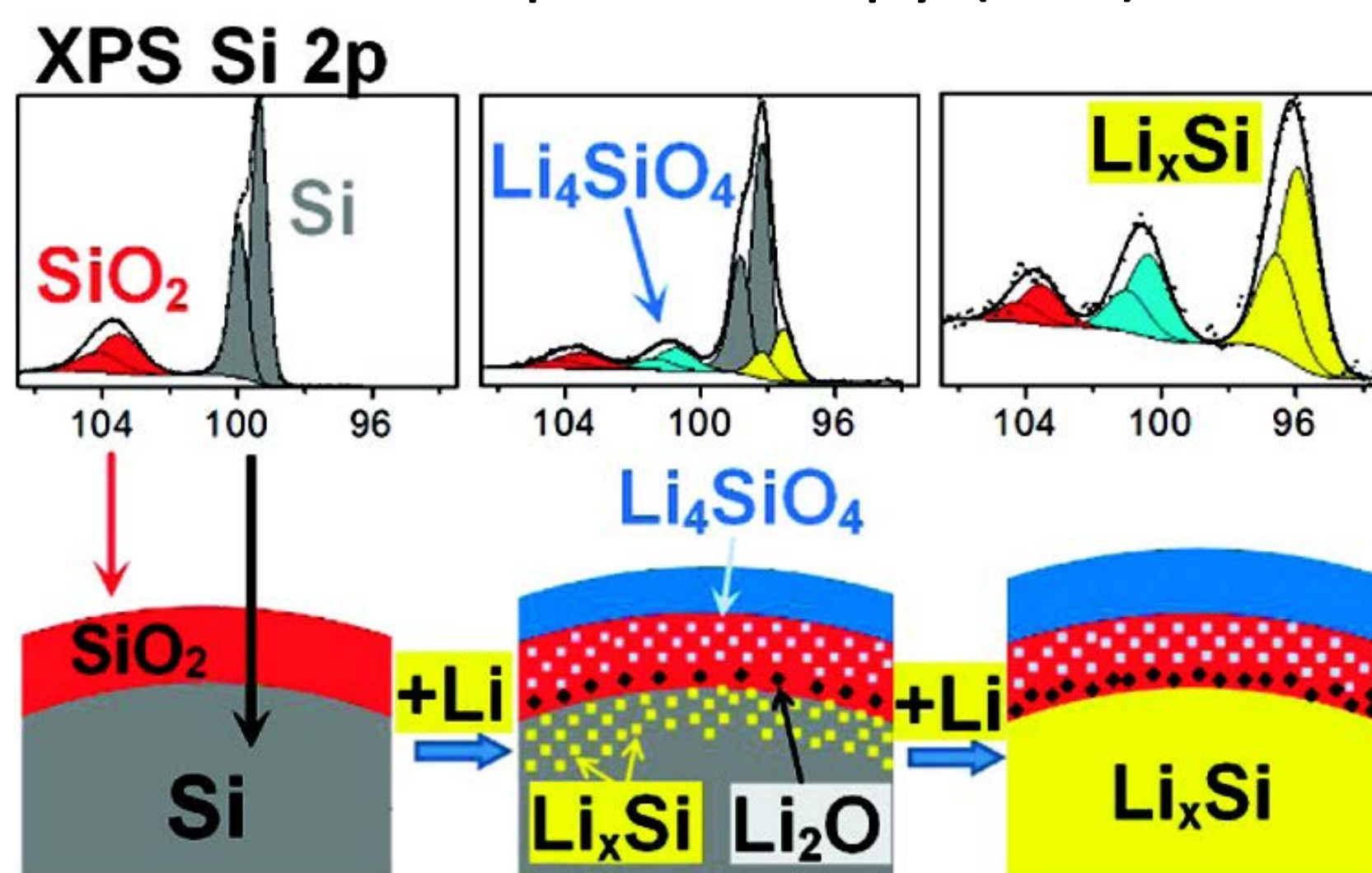
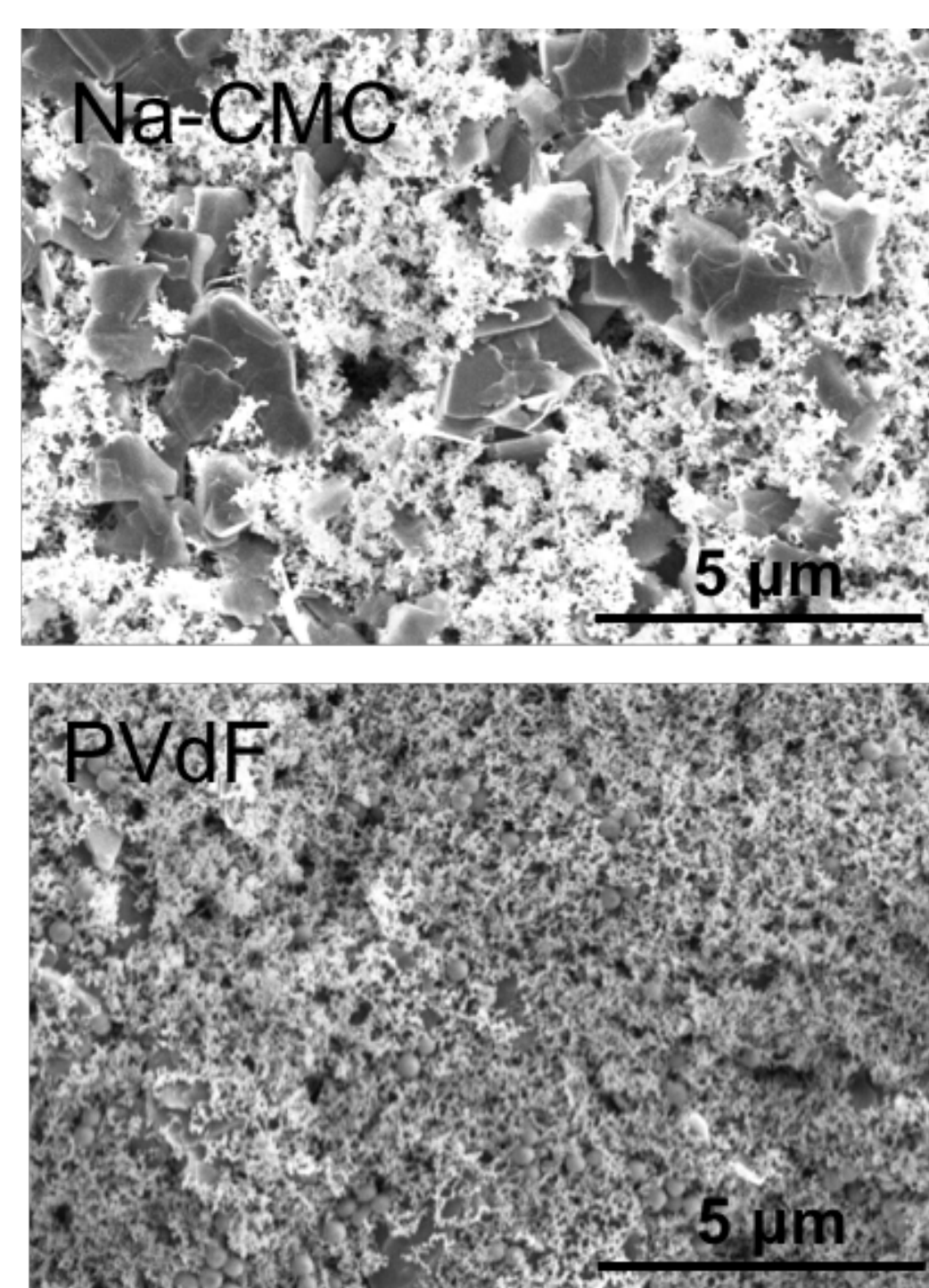
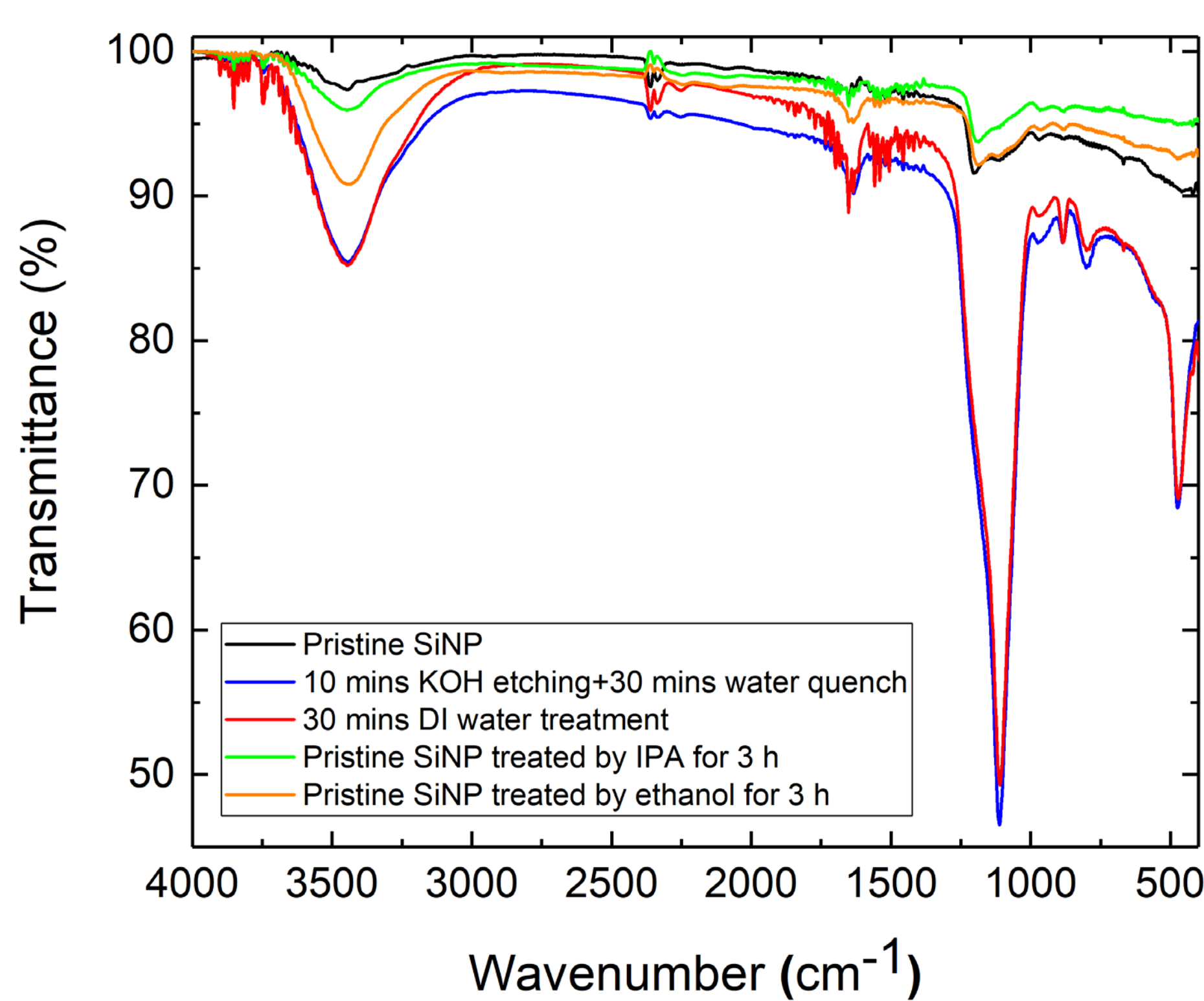


Figure 1: Mechanism of SEI formation upon discharge.

Solvent-Binder Dilemma

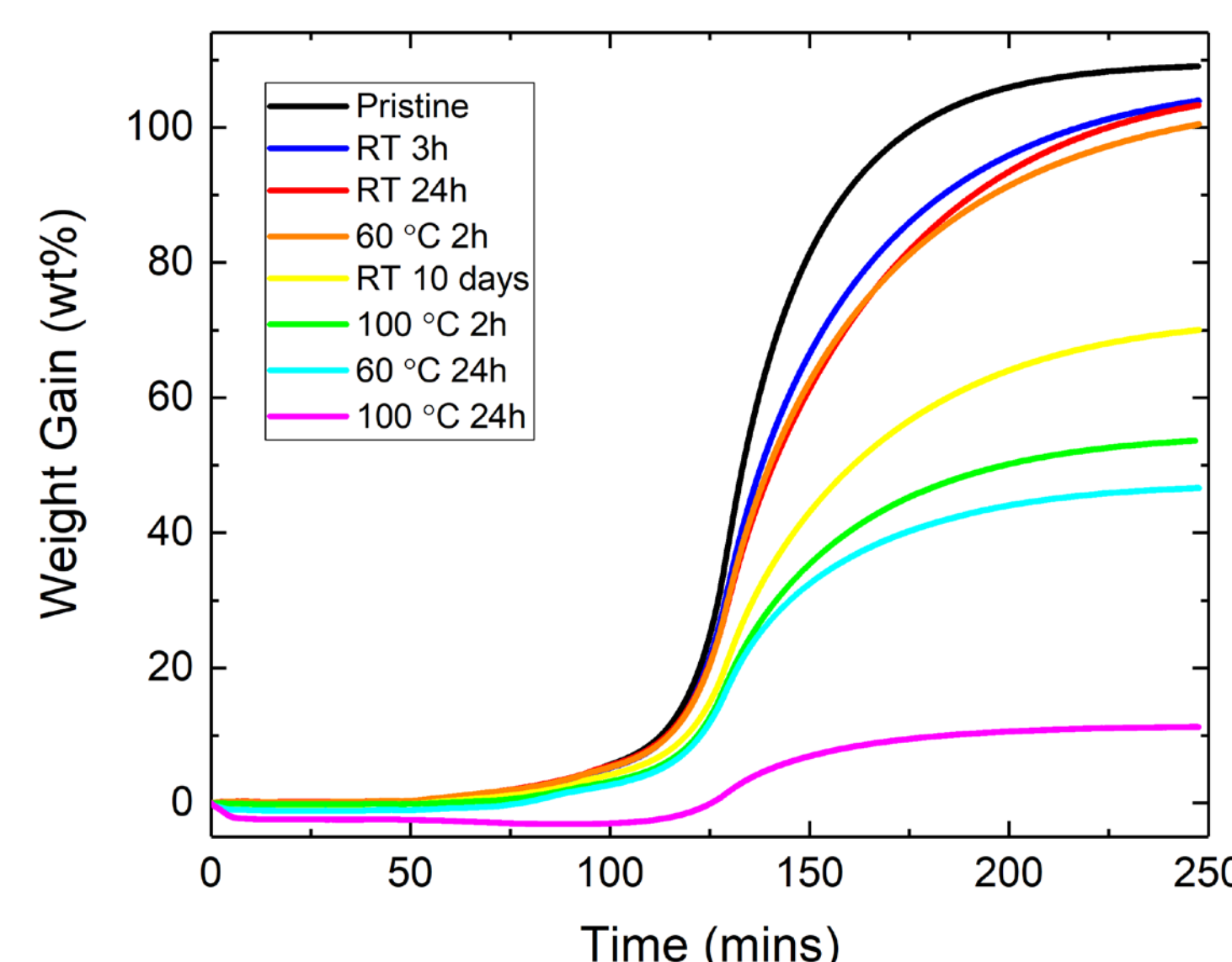


Binder Type	Solution Type	ICE (%)	50 th Cycle Capacity Retention (%)
Na-CMC	DI water	85.0	87.8
PTFE	DI water	76.1	78.8
PVdF	IPA	69.1	65.1
PAA	IPA	72.6	83.8
PAA	DI water	82.6	91.4

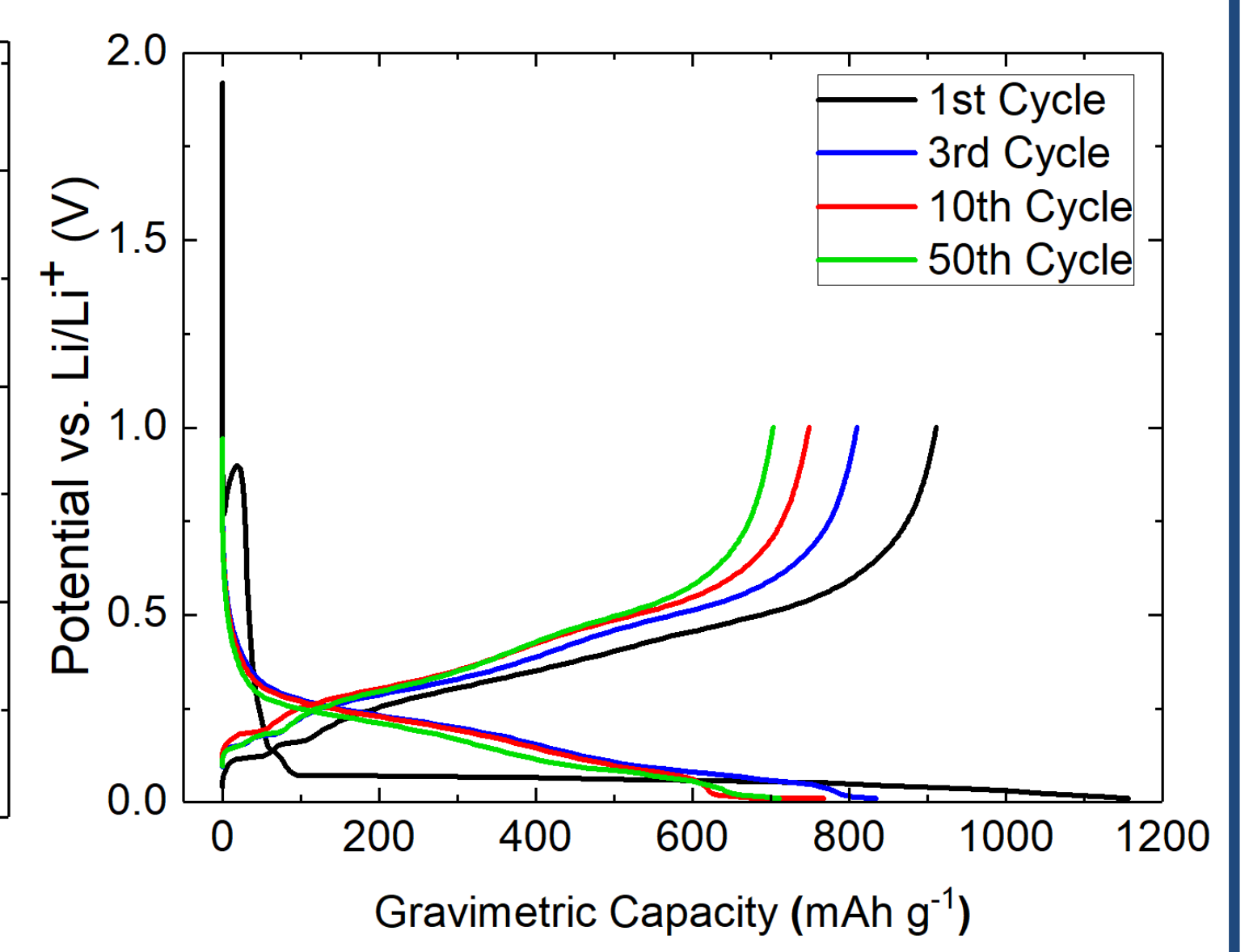
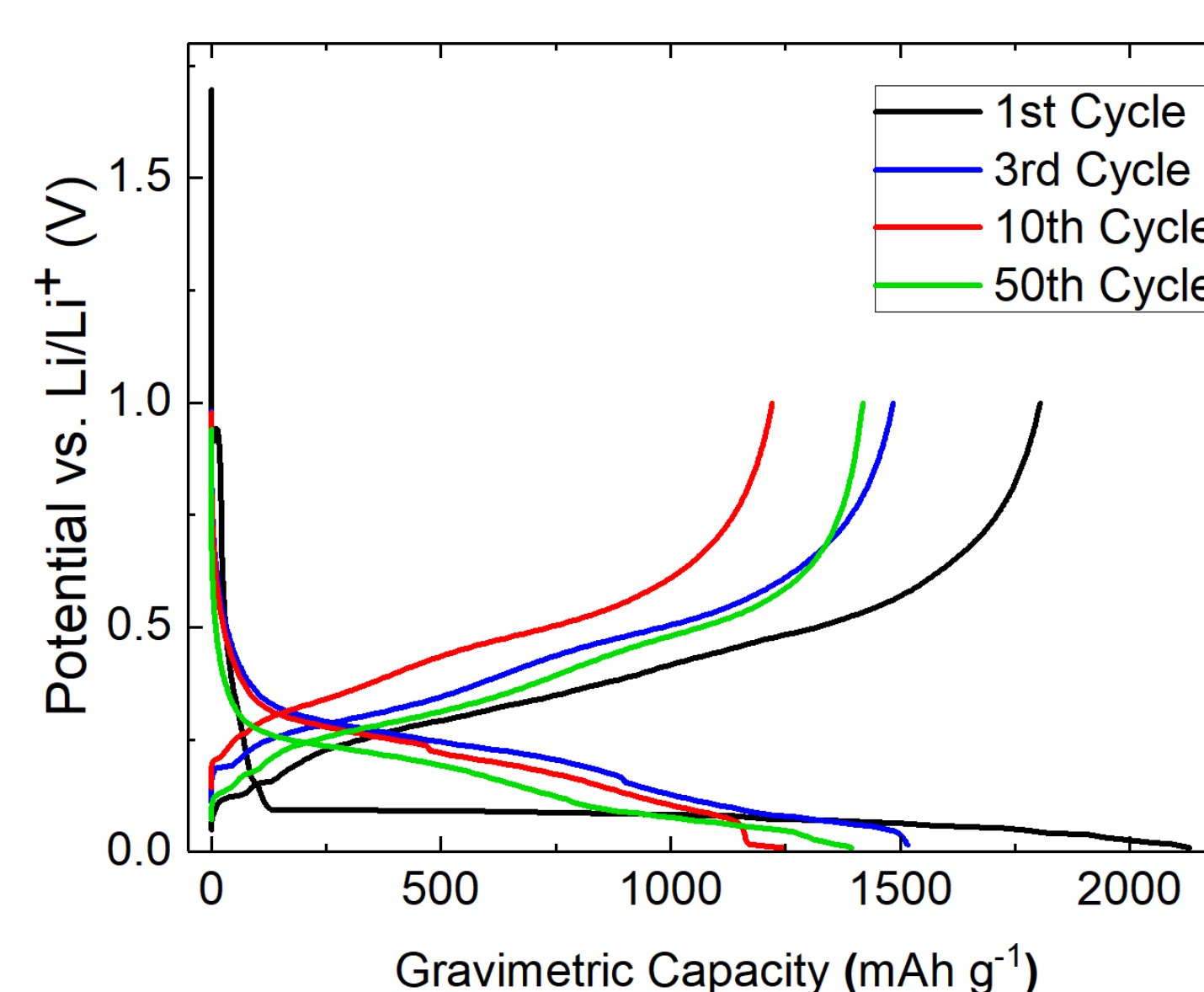
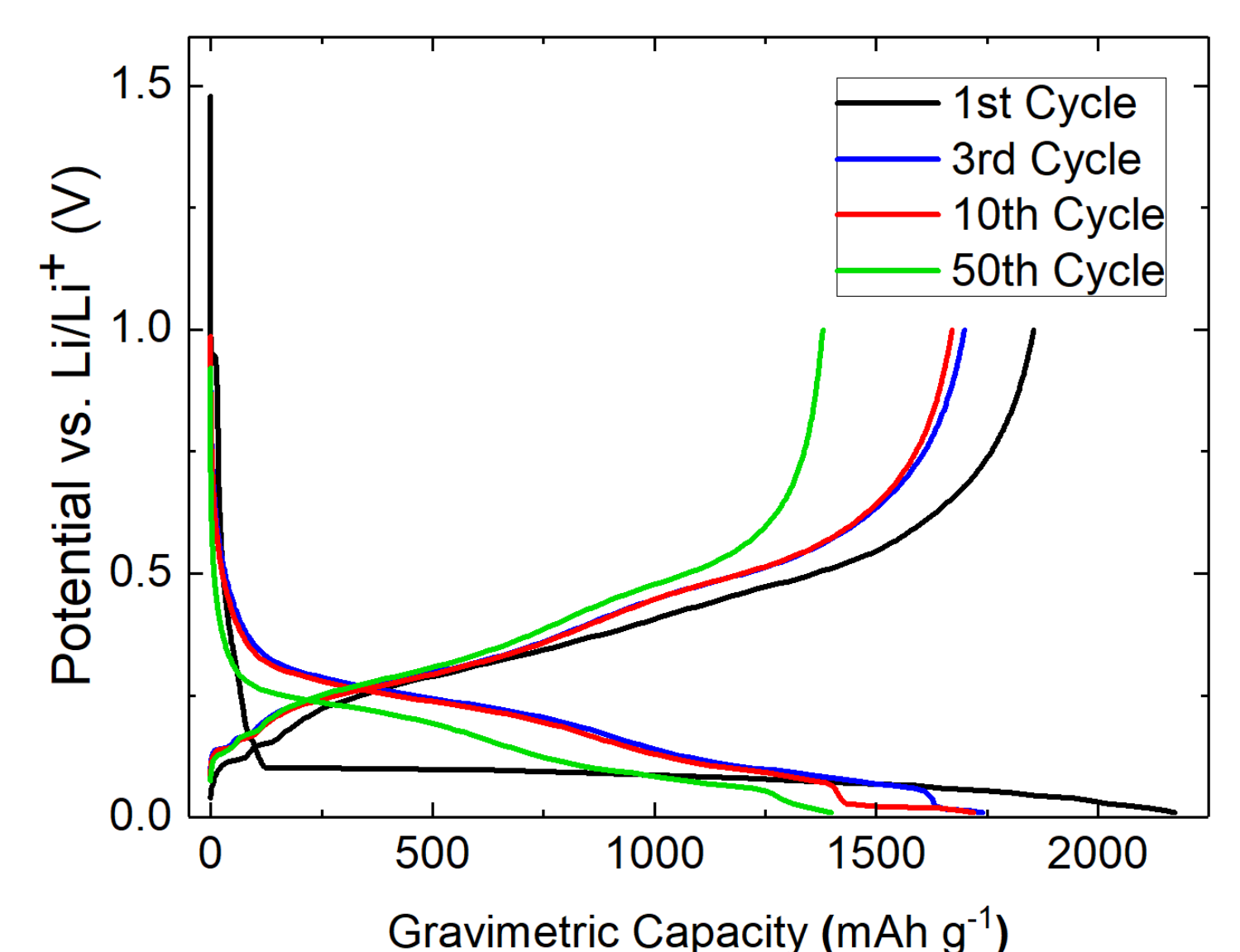
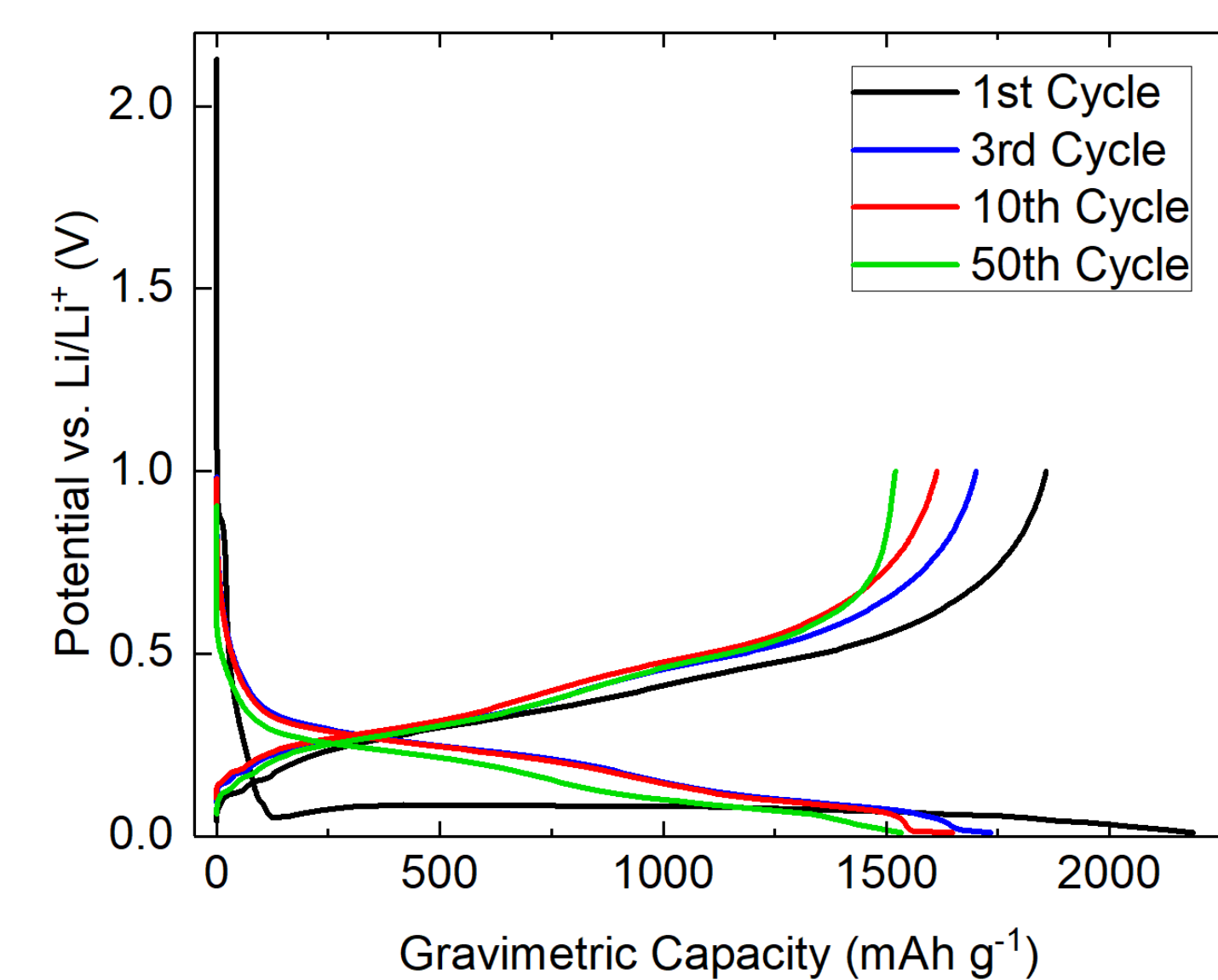
References

- [1] A. Herold, *et al.*, *Carbon*, 13(4): 337-345, (1975)
- [2] X. Liu, *et al.*, *ACS Nano*, 6(2): 1522-1531, (2012)
- [3] A. Toudjine, *et al.*, *J. Electrochem. Soc.*, 6(2): 1522-1531, (2012)
- [4] B. Philippe, *et al.*, *Chem. Mater.*, 24(6): 1107-1115, (2012)

Race Against Time



Normally the electrode slurry is prepared at room temperature (RT), which worth carrying out electrochemical characterisation to check the LIB performance with different oxide content resulted from different water pre-treatment time.



SiNP Treatment	Oxide Content (wt%)	ICE (%)	50 th Cycle Capacity Retention (%)
Non	5.0	85.0	87.8
RT 3h	10.1	85.4	80.0
RT 24 h	10.7	84.7	85.4
RT 10 days	44.0	78.8	82.0

Summary

The LIB performance is not significantly affected when the oxide content of the SiNPs is less than 10 wt%, corresponding to a layer thickness of circa. 1.3 nm, whereas larger oxide content severely reduces initial Coulombic efficiency and gravimetric capacity. Na-CMC is so far the best binder for SiNPs and graphene (conductive additive), but electrode slurry must be coated within 24 h.

Acknowledgements