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Electrode Engineering: Impact of Processing and Design towards Performance of nano-Silicon Anodes

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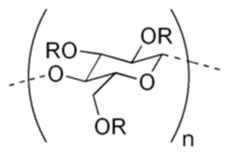
Motivation

- Silicon based anode materials for Lithium-Ion Batteries (LiBs) have high specific capacity of 3590mAh/g_{Si} at room temperature.
- Large volume changes of up to 400% occur during alloying.
- Mechanical cracking and pulverization can be overcome by using nano-sized particles [1].
- Polyvinylidene Fluoride (PVDF) cannot sustain the large stress induced in Si-based electrodes. Rapid degradation and loss of capacity are the consequence [2].
- Carboxymethyl Cellulose (CMC), Alginic acid from brown algae and Polyacrylic Acid (PAA) based binder matrices can considerably improve cycle life [2, 3, 4].
- Systematic, standardized experiments are required to compare different binders under application-related conditions [5].

Binding Mechanism and Electrode Structure

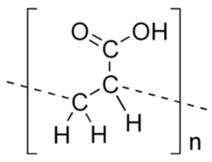
- CMC, PAA and Brown Algae have high numbers of carboxy groups (–COOH).
- –COOH groups create reversible bonds at the SiO_x particle interface.
- Bonds can be re-established after breaking.
- 'Self-healing' effect of the binder matrix.

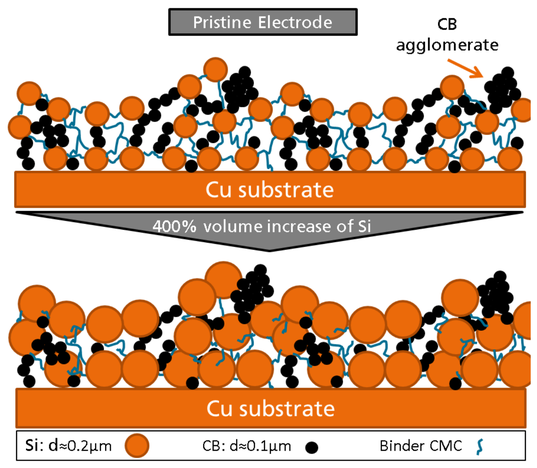
CMC



R = H or CH_2CO_2H

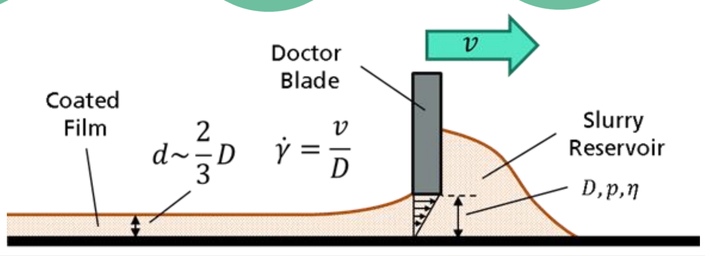
PAA



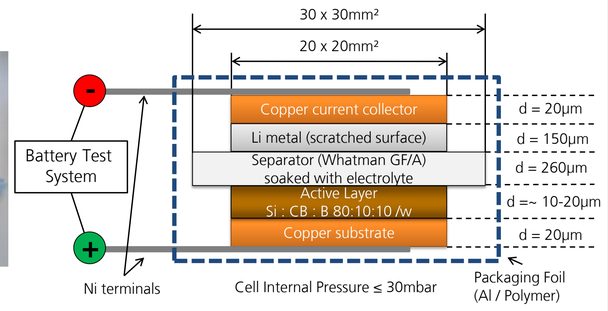


Electrode Processing

- 2 nano-Si powders and 6 binders investigated.
- Various mixing steps for good dispersion of nano particles.
- Adjustment of viscosity and doctor blade gap width to obtain loading of 1$mg_{coating}$/cm² (~2.5 mAh/cm²).



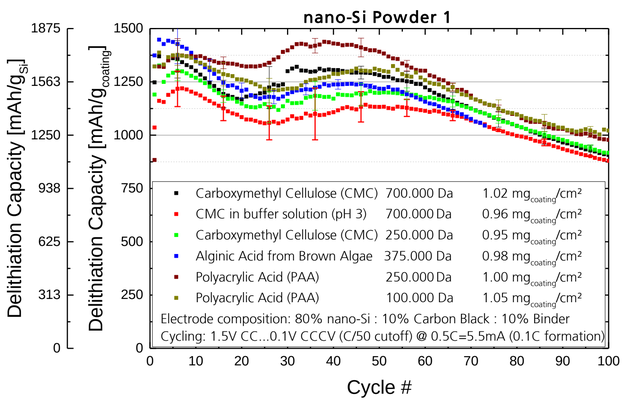
Cell Assembly

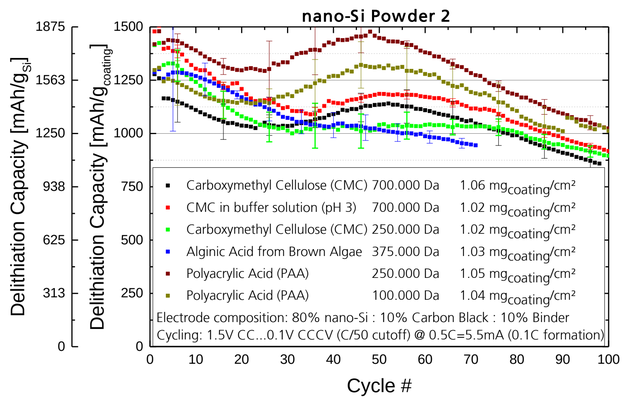


- Half cells vs. Li, Coffee Bag cell type
- Electrolyte: 1M LiPF6 in DEC:EC 1:1 + 2% vinylene carbonate

Results

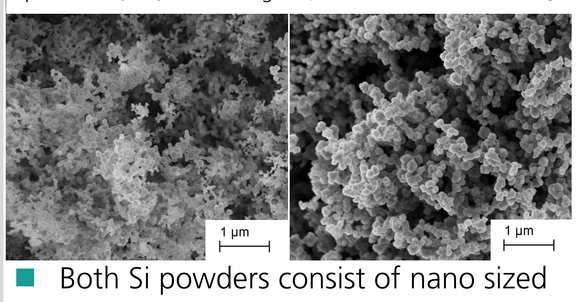
Equally Loaded Electrodes





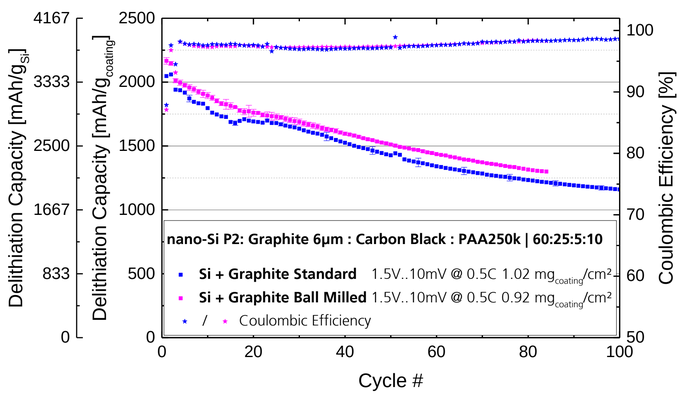
Powder Analysis

Nano-Si powder 1		Nano-Si powder 2	
Oxygen content	1.8±0.2%	Oxygen content	0.8±0.1%
Spec. Surf. (BET)	29.6 m²/g	Spec. Surf. (BET)	16.8 m²/g



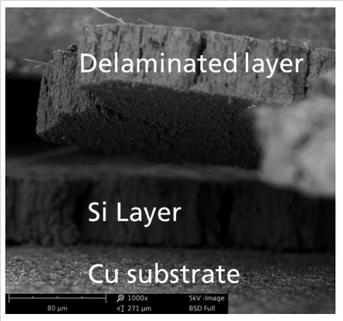
- Both Si powders consist of nano sized spherical particles.
- Particle diameter is smaller in powder 1.
- Equal, application related loadings were produced (1mg/cm² ± 10%).
- PAA-based binders show highest capacity within study.
- Capacity degradation is almost independent of binder and nano-Si powder type.

Graphite Addition

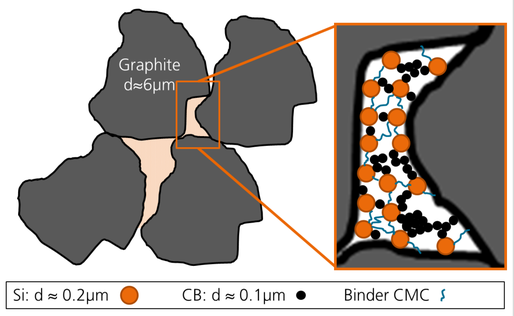


- Best result from previous experiments repeated with
  - 60% Si content
  - 25% graphite addition
  - extended voltage window
- Capacity >1000mAh/$g_{coating}$ (>1700mAh/g_{Si}) for >100 cycles.
- Ball milling of Si and Graphite leads to slight increase of capacity.

Discussion



- Nano-Si particles do not suffer from pulverization during cycling.
- CMC and PAA are suitable binders for nano-Si based anodes.
- Capacity degradation is attributed to
  - Mechanical delamination of coating layer from Cu substrate
  - Possible SEI growth and electrolyte depletion
- Reducing Si content and adding graphite particles alleviates mechanical stress within layer.
- Ball milling improves dispersion and creates thin carbon coating on Si particle surfaces.
- Shear at Si layer/ Cu substrate interface is still too high to avoid delamination.



Conclusion

- Equal loading of electrodes is important to obtain comparable results.
- Nano-Si particles can sustain repeated lithiation / delithiation for more than 100 cycles.
- CMC and PAA are suitable binders for nano-Si based battery anodes.
- Choice of binder and Si powder influences extractable capacity.
- Long term capacity degradation is almost identical for all binders and Si powders compared here.
- Mechanical stress within electrode must be alleviated to improve long term stability.

References

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