Influence of Binder Properties on Performance of Si-Based Anodes for Li-Ion Batteries

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INTRODUCTION

Since their 1990 market debut by Sony, Li-ion batteries (LIBs) have become a popular energy storage platform in portable electronics. Electric vehicles powered by LIBs have also experienced recent commercial success, but they are currently limited to short range commutes due to the low capacity of present-day electrodes (e.g., the graphite used as the anode material). Silicon is a promising candidate for next generation LIB anodes due to its high theoretical capacity (3,576 mAh/g), which is an order of magnitude greater than that of graphite (372 mAh/g). The use of Si anodes has been hindered by complications arising from Si volume changes (~400%) during battery charging and discharging. These severe volumetric swings ultimately lead to electronic isolation of Si particles, an unstable solid-electrolyte interface, and poor capacity retention.

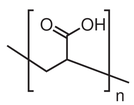
OBJECTIVES

Characterize the effectiveness of different polymer binders in Si based anodes for Li-ion batteries.

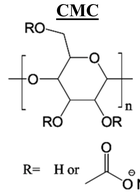
Investigate polymer crosslinking as an approach to maintain intimate contact between Si nanoparticles and the polymer binder.

Structures of polymer binders investigated in this study.

PAA



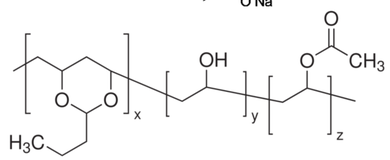
CMC



PVDF

R= H or

PVBAA



APPROACH

Slurries containing Si nanoparticles (20 nm), carbon black, and a polymer binder were cast onto copper foil. All anodes contained 60 wt% Si, 20 wt % C, and 20 wt% binder and were characterized in CR2032 Li-ion half cells.

CR2032 Construction and Characterization

Anode: Si based slurry on copper foil

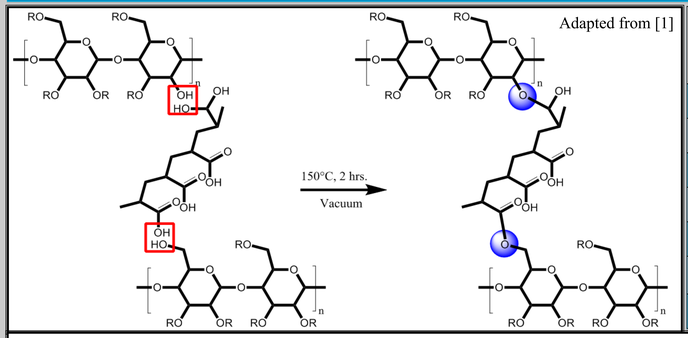
Counter electrode: Li metal

Electrolyte: 1.0 M $LiPF_6$ in 1/1/1 EC/DEC/DMC (ethylene carbonate/ diethyl carbonate/dimethyl carbonate) by volume with a 5 wt% vinylene carbonate additive

Voltage Range: 0.015-1.5V

Constant Current: 0.1C

POLYMER CROSSLINKING

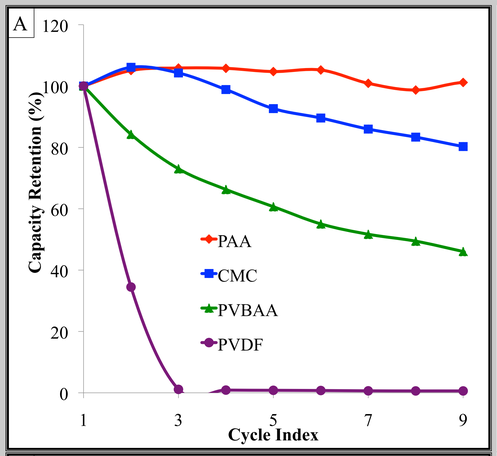


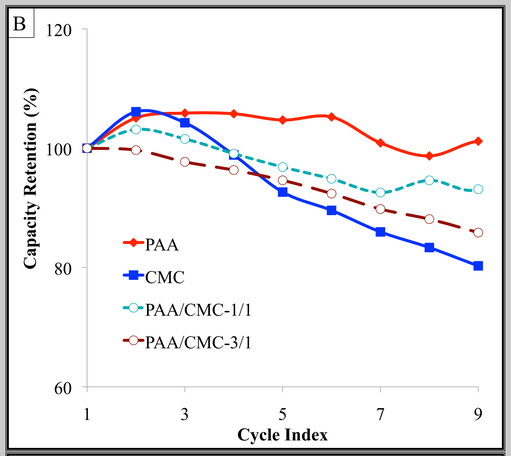
POLYMER FILM	SWELLING IN SOLVENT (wt%)
PAA	∞
CMC	∞
PVBAA	∞
PAA/CMC-1/1	19
PAA/CMC-3/1	32
PAA/PVBAA-1/1	292
PAA/PVBAA-4/1	376

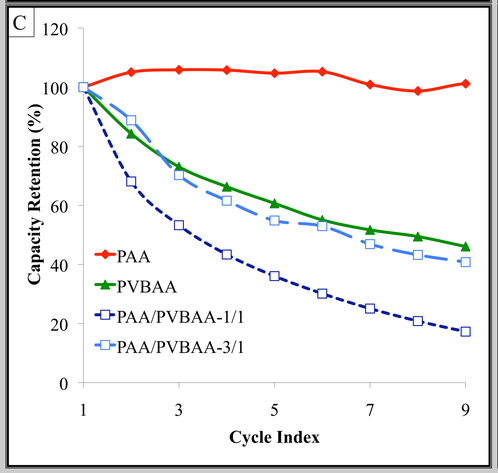
Reaction Scheme: PAA/CMC crosslinking was performed under vacuum at 150˚C for 2 hours. An analogous reaction was performed for PAA/PVBAA systems (not shown) under the same conditions.

Table: Crosslinking was confirmed through polymer swelling experiments.
- Polymer films (without Si or C) were soaked at room temperature for 3 hours in water (PAA, CMC) or methanol (PAA, PVBAA).
- Individual polymers fully dissolved in solvent.
- Crosslinked polymer films exhibited limited swelling, which indicates successful crosslinking.
- Increased PAA content decreased the crosslinking effectiveness.

ELECTROCHEMICAL PERFORMANCE







Anode capacity retention during battery cycling.

A: Uncrosslinked polymer binders
- PAA and CMC systems exhibited high initial capacities (1,800 and 1,400 mAh/g, respectively).
- Anodes containing PVBAA and PVDF showed very low capacities (6 and 225 mAh/g, respectively).
- PAA and CMC binders yielded the best capacity retention.

B: Crosslinked PAA/CMC binders
- Crosslinking did not significantly impact anode performance.
- Anodes with PAA exhibited the best capacity retention.

C: Crosslinked PAA/PVBAA binders
- Crosslinking did not improve capacity retention.
- Anodes with PAA exhibited the best performance.

POLYMER-ELECTROLYTE SWELLING

POLYMER FILM	SWELLING (wt%)	INITIAL CAPACITY (mAh/g total)	CAPACITY RETENTION AFTER 9 CYCLES (%)
PAA	2	1,807	101
CMC	2	1,388	80
PVBAA	15	6	46
PVDF	19	225	1

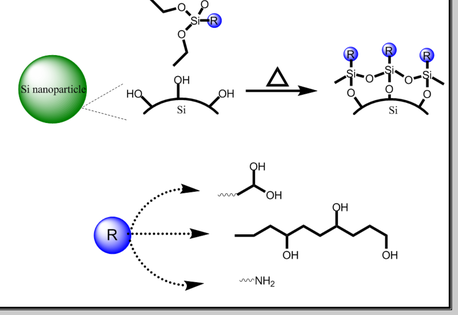
Swelling was determined after soaking polymer films (without Si or C) at room temperature in propylene carbonate for 3 hours.
- PAA and CMC systems exhibited low swelling.
- PVBAA and PVDF showed moderate swelling (>15%)

Binders which swelled less in propylene carbonate showed superior battery performance
- Higher initial capacity
- Better capacity retention

FUTURE WORK

The findings of this study will be used as reference data for future work with electrospun Si/C/ polymer nanofiber electrodes. This future investigation will determine how electrode morphology affects anode stability.

A separate study will use silane chemistry to functionalize silicon nanoparticles. Silane functional groups will be chosen to maintain intimate contact between Si nanoparticles and the polymer binder during battery cycling.



CONCLUSIONS

PAA/CMC and PAA/PVBAA systems were successfully crosslinked.

PAA and CMC are promising binders for Si based anodes
- Low swelling in propylene carbonate (~2%)
- High initial capacity (>1,000 mAh/g total) and moderate capacity retention

PVBAA and PVDF are poor binders for Si based anodes
- Very low capacities (<300 mAh/g total) and poor capacity retention

Thermally crosslinked binders did not enhance anode stability
- Limited electrolyte absorption may limit the effectiveness of crosslinks

ACKNOWLEDGEMENTS

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REFERENCES

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