

Reversible High Capacity Si Nanocomposite Anodes enabled by Molecular Layer Deposition

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The development of high-energy lithium-ion batteries (LIBs) requires the incorporation of materials such as silicon (Si) as a replacement for the commercialized graphite anode.^[1] Si is known for its high specific capacity and natural abundance.^[1, 2] Accommodating 3.75 mole Li per mole of Si ($\text{Li}_{15}\text{Si}_4$) for a theoretical capacity of 3579 mAh g^{-1} at room temperature, Si has become one of the most investigated materials for LIB's anodes.^[3, 4] Despite Si's inherent potential, progress towards a commercially viable Si anode has been impeded by Si's fast capacity fade, poor ionic transport and low coulombic efficiency (CE).

The high volumetric changes of $\sim 300\%$ for Si upon lithium alloying and de-alloying is very extreme. Even though pulverization of the Si particles themselves due to volume changes has been solved by integrating particles smaller than 150nm ^[5], cracking and broken connections within the electrode's network have become the biggest challenge in realizing a Si-based anode. This high volume expansion/contraction is beyond the limits of most coating materials, including the use of surface modifications such as atomic layer deposition (ALD) of metal-oxides and carbon coatings.^[6, 7] Earlier work done by our group^[8] and by others researchers^[9, 10] on flexible coatings/films for Si-based electrodes has shown that surface modification layers and/or electrodes' binders with elastic mechanical properties have led to remarkably improved cycling stability of Si-based anodes. These previous studies have concluded that a necessary condition for the stabilization of high capacity anodes is the formation of elastic, flexible surface coatings/films that can accommodate the volume changes of the anode.^[8-10] To meet the challenge of the high volumetric changes, we have fabricated a new flexible molecular layer deposition (MLD) film as a surface modification for high capacity Si nanocomposite anodes.

We have examined a new family of flexible metalcones films via MLD known as alucones. In our work we used alucone MLD films based on reactions of inorganic trimethylaluminum (TMA) ($\text{Al}(\text{CH}_3)_3$) and organic glycerol (GL) polyols ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$) precursors to form poly(aluminum glycerol) [$(-\text{Al}(\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH})_x)_n$] polymers.^[11] Figure 1 shows the structure of the aluminum alkoxide alucone polymer used in this work. By coating nano-Si composite anode electrodes with alucone polymer films via MLD using TMA and GL, we show that it is possible to cycle these conventional nano-Si electrodes for over 50 cycles with capacities in excess of 1000 mAh g^{-1} and CEs of over 99.5% (Figure 2).

References

- [1] U. Kasavajjula, C. Wang, a. J. Appleby, Journal of Power Sources 2007, 163, 1003-1039.
- [2] J.-M. Tarascon, M. Armand, Nature 2001, 414, 359-367.
- [3] B. A. Boukamp, G. C. Lesh, R. A. Huggins, Journal of The Electrochemical Society 1981, 128, 725-729.
- [4] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, Journal of Power Sources 2001, 97-98, 235-239.
- [5] X. H. Liu, L. Zhong, S. Huang, S. X. Mao, T. Zhu, J. Y. Huang, ACS Nano, 2011, 6, 1522-1531.
- [6] L. A. Riley, A. S. Cavanagh, S. M. George, Y. S. Jung, Y. Yan, S.-H. Lee, A. C. Dillon, Chem. Phys. Chem., 2010, 11, 2124-2130.
- [7] M. Gu, Y. Li, X. Li, S. Hu, X. Zhang, W. Xu, S. Thevuthasan, D. R. Baer, J.-G. Zhang, J. Liu, C. Wang, ACS Nano, 2012, 6, 8439-8447.
- [8] D. Molina Piper, T. A. Yersak, S.-B. Son, S. C. Kim, C. S. Kang, K. H. Oh, C. Ban, A. C. Dillon, S.-H. Lee, Adv. Energy Mat., 2013 (in press).
- [9] G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V. S. Battaglia, L. Wang, W. Yang, Advanced Materials 2011, 23, 4679-83.
- [10] D. Aurbach, Journal of Power Sources, 2000, 2, 206-218.
- [11] B. H. Lee, B. Yoon, A. I. Abdulagatov, R. A. Hall, S. M. George, Adv. Funct. Mat., 2013, 23, 532-546.

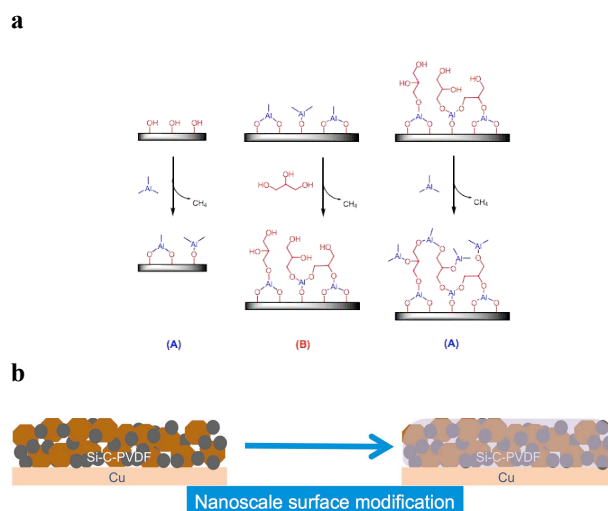


Figure 1: (a) Static AIGL MLD chemistry and (b) schematic of AIGL MLD surface modification process on nano-composite electrode.

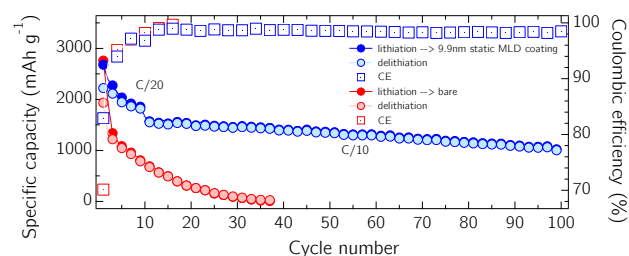


Figure 2: Cyclic capacity and CE of Si nanocomposite anodes (nSi:AB:PVDF) coated with static AIGL MLD (blue circles and squares) and uncoated/bare (red circles and squares).