Carbon-Silicon Composite Anodes for Automotive Batteries

Mohan Karulkar, Rachel Blaser
Ford Motor Company
MD 3179, 2101 Village Rd, Dearborn MI 48121

Silicon represents an attractive alternative to graphite for the anode material in automotive batteries, with over 3500 mAh/g theoretical capacity, but the large volume change upon lithiation (up to 300%) is a major limitation to cycle life. Silicon composite materials are also of interest, particularly carbon-silicon (C-Si). At the sacrifice of some capacity, the addition of graphitic carbon appears to buffer the volume change and stress.[1] The use of graphite may also lend some Li capacity back. In the present study, we assessed the feasibility of such a C-Si system, using modeling and materials engineering.

A design model was developed to analyze the automotive viability of C-Si, compared to a subset of USABC long-term electric vehicle performance targets (Table 1).[2] In order to estimate battery performance, a C-Si cathode was paired with a hypothetical air cathode of previous design.[3] Given electrode characteristics in Table 2, it was found that USABC targets could be met with a capacity of 1475 mAh/g and a current density of 10.9 mA/cm^2. These results establish key metrics for C-Si, and in particular highlight the necessity of improved current density. Strategies included optimizing milling conditions and Si content, and reducing interfacial resistance and stress.

C-Si powder was fabricated using high energy ball milling, similar in method to Kumta et al,[4] with optimized milling and composition. Silicon and graphite were milled in a solution of N-methylpyrrolidinone (NMP) and polyacrylonitrile (PAN) to prevent formation of silicon carbide, after which the slurry was baked at 800C under argon. The PAN-NMP component was pyrolyzed, and the final material was a mixture of C-Si composite and amorphous carbon.

C-Si powder was combined with NMP, C45 carbon black, and polyvinylidene fluoride (PVDF), and electrodes were fabricated by tape casting the slurry on a copper foil. Electrodes were assembled in Swagelok-style cells under Ar, and cycled using a Celgard 2400 separator, lithium counter electrode, and 1M $LiPF_6$ electrolyte in 3:7 EC/DEC. In order to improve adhesion and interfacial conductivity, a conductive layer technique similar to Lee et al[5] was also investigated, in which a thin film of PVDF and graphene (1%) was cast on the copper foil prior to casting the C-Si slurry. Anodes were also made for comparison using powder provided by Kumta et al.

Figure 1 shows adhesion results of tack testing with and without a conductive layer. 100% of the anode was lost from as-is copper foil, whereas only 25% was removed from the sample containing a conductive layer. Figure 2 shows discharge capacity for samples with and without a conductive layer, cycled at 0.7 mA/cm^2, from 1.2-0.02 V. A consistent improvement of 400 mAh/g is seen across 25 cycles. Figure 3 shows performance of anodes made using provided powder with 8% Si and a milling ball:powder ratio of 10:1, versus in-house C-Si with 25% Si and milling ratio of 4:1. Both samples utilize a conductive layer, and were cycled at 0.7 mA/cm2 from 0.02 to 1.2 V. The 25% Si sample shows ~500mAh/g greater capacity.

Table 1: C-Si performance vs USABC targets.

Criteria	Units	Target	Calculated	Current
Specific Energy	Wh/kg	400	858	597
Volumetric Energy	Wh/L	600	601	351
Specific Power	W/kg	800	1712	161
Volumetric Power	W/L	1200	1200	95

Table 2: Design model parameters.

Parameter	Value
Anode Thickness (cm)	0.0093
Anode Loading (g/cm2)	0.003
Cathode Thickness (cm)	0.0075
Cathode loading (g/cm2)	0.005
Separator	Celgard 2400

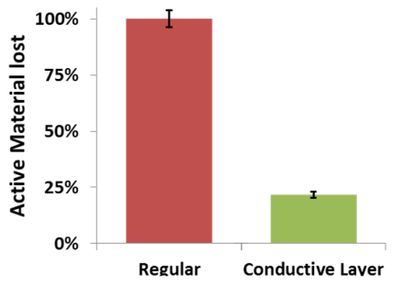

Figure 1: Tack testing showing 75% improved adhesion when using conductive layer.

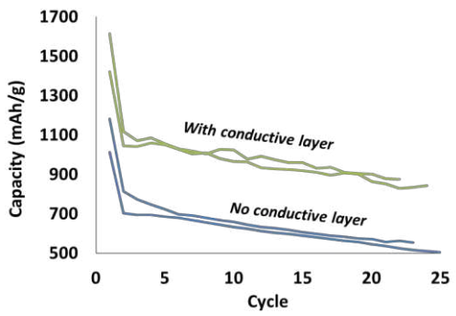

Figure 2: Performance of C-Si with and without a conductive layer. Cycled at 0.7 mA/cm2, from 0.05-1.2V.

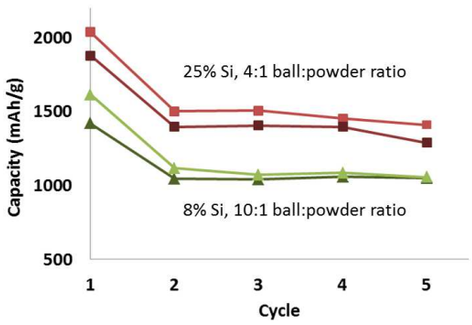

Figure 3: Performance comparison between conductive-layer electrodes using as-provided 8% Si / 10:1 milling ratio powder, and Ford 25% Si / 4:1 fabricated powder.

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[1] Wei-Jun Zhang , J. Power Sources, **196**, 13–24 (2011).
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[4] M.K. Datta, P.N. Kumta, J. Power Sources, **194**, 1043–1052 (2009).
[5] S. Lee, E. Oh, J. Power Sources, **In Press** (2012).