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Baseline Si electrode fabrication and performance for the Battery for
Advanced Transportation Technologies (BATT) Program

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Abstract

Baseline Si electrodes were developed and characterized based on spherical Si nanomaterials. Silicon (Si) with a designed nanostructure has attracted much attention as potential anode materials for lithium-ion batteries due to its high gravimetric specific capacity. Because of a resulted poor tap density of Si from the electrode while using nano-sized Si and also from including other additives like conductive carbon and binder, it is difficult to maintain a high loading of active materials at the anode side in lithium-ion batteries. In this report, we aim to investigate how the thickness and Si material loading of Si-based electrode influences the cycling performance, rate performance and impedance. We also discuss the variation of gravimetric, area and volumetric capacity along with increasing of electrode thickness and Si material loading. It is found that with a thinner electrode of 7 μm the volumetric capacity could reach up to 920 mAh/cm³ but a poor area capacity of 0.7 mAh/cm², while a thicker one of 33 μm enables to provide a high area capacity up to 1.5 mAh/cm² and gives a volumetric capacity less than 500 mAh/cm³. A cell operated under 0 °C shows a gravimetric capacity of 2000 mAh/g after 60 cycles.

Keywords

Silicon, lithium-ion batteries, electrode thickness, electrochemical performance, low temperature batteries

Introduction

Silicon (Si) has been extensively studied as one of the most promising anode for Li-ion batteries because of its delivering a greater theoretical gravimetric specific capacity (4200 mAh/g) over the conventional graphite anode (372 mAh/g).¹⁻² For a volumetric comparison, graphite has a theoretical volumetric capacity about 850 mAh/cm³. For a typical 20 vol % Si electrodes discussed in Beattie's previous report, it has a volumetric energy density of 1668 mAh/cm³.³ The gravimetric energy density of Si electrode at the laminate level can easily exceed 3000 mAh/g (excluding the current collector), based on classic electrode design, which includes 90% (by weight) graphite, 10% of polymer binder and acetylene black (AB) conductive additive, and 30% porosity. This would be ten times higher than that of the graphite based electrode with the same composition and design. Practical volumetric energy density of graphite electrode is around 400 mAh/cm³ using classic electrode design.⁴ Switching from graphite to Si could potentially improve the volumetric energy density in lithium-ion batteries beyond 1000 mAh/cm³.⁴⁻⁶

As forming a Li_{4.4}Si alloy from lithium intercalating into Si, a 320% volume expansion occurs when full lithiation on Si.^{2, 7-8} This large volume change lead to a destructive pulverization of Si as well as electrical contact loss between active materials, which eventually cause a fast capacity fading of battery.^{2, 9-10} Si nanostructure designing by taking the advantages of large surface area and porosity, greatly alleviates the mechanical stress during volume changing as well as enhances

the electronic connections. The successful examples included Si nano particles,¹¹⁻¹² Si nanowires,^{5, 13} Si/C nanocomposites,¹⁴ and nanoporous Si¹⁵⁻¹⁸ which effectively addressed the challenge of volume change during lithiation and gave a stable cycling performance of batteries. Unfortunately, such a nano Si structure along with a high porosity packed inefficiently with a low stacking density, which would lower the volumetric energy density, and need to increase the loading of other components including binder and conductive agent leading to more side reactions. High energy density battery with an ordered-structure like Si nanowires has been demonstrated to exhibit a high volumetric energy density in lithium-ion batteries, especially combining with carbon to form Si/C composite electrode. Very few examples have been reported on achieving both a high area and volumetric capacity so far. Cui and coworker first developed freestanding nanocomposites made of carbon nanofibers (CNFs) and silicon nanowires (SiNWs) as metal current collector-free anode platforms. This achieved an improved areal capacity up to 5 mA/cm² and a corresponding volumetric capacity of 1429 mAh/cm³.⁴ Later on, Cho reported a new architecture consisting of SiNWs internally grown from porous graphite, providing more free spaces to accommodate volume expansion of internally grown Si during cycling and facilitate electron transport as well. With this strategy, the electrode has a high density of 1.5g/cm³ and the prepared battery exhibits a high volumetric capacity of 1363mAh/cm³ with high initial coulombic efficiency over 90%.⁵ Very recently, Cui's group designed a pomegranate-inspired nano structure with void space around single Si nanoparticles in an encapsulated thicker carbon layer, which enable to leave a

buffering room for Si expansion and contraction. After continued lithiation/delithiation, the solid-electrolyte interphase (SEI) layer remained stable with high capacity retention over 97% after 1000 cycles. And the cycling performance remained stable even when the area capacity increased above 3mAh/cm².⁶

Considering complex manufacturing process and high cost of nano-sized Si, and Si large volume expansion, it is very challenging to develop a Si based material and electrode assembly approach for a practical high capacity Si electrode. In this study, we selected commercial scale pure nano-sized silicon particles, sodium carboxymethylcellulose (NaCMC) binder and acetylene black to make baseline composite electrodes. Charge/discharge cycling performance, rate performance has been studied while applying different thickness of anodes, especially a full discussion on variation of corresponding gravimetric, area and volumetric specific capacity. This effort is part of the US DOE's Battery for Advance Transportation Technologies program R&D effort to develop advanced high capacity Si anodes. Baseline Si based electrodes developed at Lawrence Berkeley National Laboratory provide a benchmark for the comparison study of variety of the materials and electrodes developed under the BATT program.

Experimental

The nano-sized Si particles were experimental sample named Si NanoGrain® from Umicore. Acetylene black as conducting agent was purchased from TIMCAL. To make a baseline electrode, a slurry including n-Si particles (50 wt %), carboxymethyl

cellulose binder (20 wt %), poly vinyl alcohol (PVA) (5 wt %) and acetylene black (25 wt %) in aqueous solution was homogenized for one hour. The uniform slurry was cast on copper foil. The thickness of electrodes was controlled by doctor blade gap to achieve the desired area capacity loading. Electrolytes were purchased from Novolyte (now part of BASF), including battery-grade lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC), diethyl carbonate (DEC) and fluoroethylene carbonate (FEC). The Baseline composition of electrolyte is 1M LiPF_6 in EC: DEC=1:1 with 10% FEC by weight. For Celgard 2500 separator membrane was purchased from Celgard. Other chemicals were purchased from Sigma-Aldrich and used without any further purification. Coin cells were prepared with lithium metal (purchased from FMC Corporation) as counter electrode. The cell fabrication process can be found in the literature.¹⁹ The coin cell performance was evaluated with a Maccor Series 4000 Battery Test System in a thermal chamber at 30 °C. The C-rate calculation of the Si based electrode is assuming the Si has the theoretical capacity of 4200 mAh/g. The voltage range for the electrochemical testing is 1V to 0.01 V. The cells were first formed at C/25 rate for 3 cycles, and cycling at C/3 lithiation rate and C/2 delithiation rate. Electrochemical Impedance Spectroscopy (EIS) were conducted on a VMP galvanostat/potentiostat (Bio-Logic). Si half cells were cycled for 50 complete cycles at a C/10 rate, followed by a half lithiation at one extended cycle and rested for 4 hours before EIS measurement. The sample cells were brought to 10 mV before impedance measurement was taken at 0.01 Hz to 0.1 MHz.

Morphology of the electrode surface was characterized using a JSM-7500F scanning

electron microscopy (SEM). High resolution transmission electron microscope (TEM) images were obtained on a Philips CM200 field emission microscope operated at 200 kV at National Center for Electron Microscopy (NCEM) at LBNL.

Results and discussions

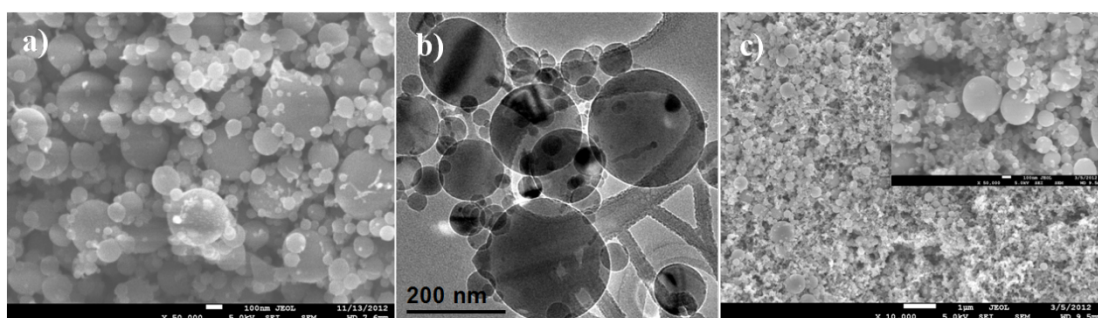


Figure 1.a) SEM and b) TEM image of pristine n-Si particles, c) SEM image of composite electrode contains 50wt% n-Si, 25wt% AB, 25wt% Binder (Inset: its high magnification image)

A commercial available n-Si nanoparticle has been selected as an active material. A corresponding laminate (or composite electrode) was made of 50wt% Si, 25wt% Acetylene black and 25 wt% polymer binder (20 wt% sodium carboxymethylcellulose (NaCMC) plus 5 wt% Poly vinyl alcohol (PVA)). The pristine Si particles have sphere structure everywhere with a large size distribution from 50nm to 200 nm both shown from SEM and TEM (Figure 1a and 1b). Prepared composite electrode has also been imaged under SEM exhibiting large porosity, which provides lots of voids for large volume expansion during charge/discharge of Si (Figure 1c and 1d). The Si particles are glued by a commercial NaCMC binder and electrical connected by AB particles.

Table 1. Thickness, Si loading and porosity of Si electrodes

Entry	Thickness	Si loading	Porosity
1	7 μm	0.24 mg/cm ²	65 %
2	17 μm	0.44 mg/cm ²	72 %
3	33 μm	0.74 mg/cm ²	78 %

Density of Si, NaCMC and AB is 2.33g/cm³, 1.59g/cm³ and 1.95g/cm³, respectively.

The electrochemical performance with different thickness of Si electrode was shown in Figure. 2. Three laminates have been prepared with the thickness of 7 μm , 17 μm , and 33 μm respectively. Corresponding Si loading and electrode porosity are calculated and listed in the Table 1. While increasing the thickness, the packing efficiency of Si particles in the electrode becomes less efficient with a larger porosity. Especially an electrode with 33 μm thickness holds a porosity of 78%, which would potentially accommodate more Si volume expansion during lithiation. For a better comparison, all cells under testing were made of cells using Li metal as the counter electrode. As seen in Figure 2a, all three cells showed a very similar capacity fading trend. In the very beginning, a slow lithiation rate of C/25 is applied for three cycles for SEI formation followed by fast cycling test. It is observed that faster capacity fading occurred at the first 20 cycles, and the cell capacity become more stable in extended 30 cycles. The thinnest electrode of 7 μm always gives the best performance of gravimetric capacity of 3750 mAh/g at a slow rate in initial, and then enables to maintain the capacity over 2700 mAh/g even after 50 cycles at faster rate. However as long as we increase the electrode thickness to thicker ones like 17 μm and 33 μm , the gravimetric capacity decreases to 2250mAh/g and 2000 mAh/g at the 50th cycle. We attribute this to poor lithium diffusion within a thicker electrode, which results some

capacity loss. In the Figure 2b, three thicknesses of electrodes all perform a high first cycle coulombic efficiency of 88%. All cells' coulombic efficiency approach 99% after only 10 cycles.

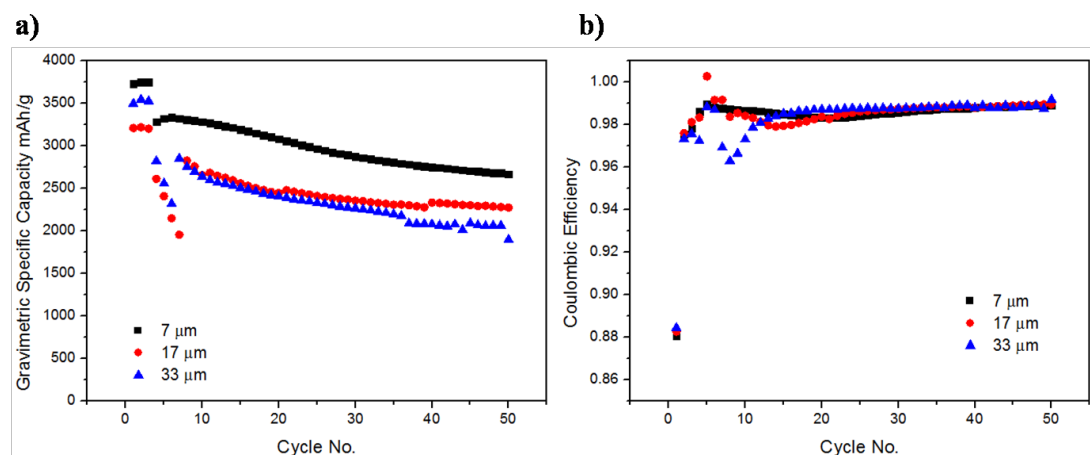


Figure 2. a) Cycling performance (Gravimetric Specific Capacity vs. Cycle No.) of n-Si/NaCMC/PVA/AB electrodes with different thickness (7 μm , 17 μm and 33 μm) and their b) corresponding coulombic efficiency.

Different thickness of electrodes represents different loading of active material. As calculated in Table 1, the n-Si loading of 7 μm , 17 μm and 33 μm electrode is 0.24, 0.44, 0.74 mg/cm^2 . The area capacity of a thin electrode (7 μm) is about 0.7 mAh/cm^2 at a rate of C/10 after 50 cycles without too much capacity fading. Its volumetric capacity is 1280 mAh/cm^3 at C/25 and 920 mAh/cm^3 after 50 cycles at C/10. A middle-thick electrode (17 μm) gives an area capacity of 1.0 mAh/cm^2 and 600 mAh/cm^3 at the 50th cycle. With further increase the loading to 0.74 mg/cm^2 (33 μm), the cell enables to be cycled at a high area capacity over 2.5 mAh/cm^2 and still can maintain a capacity of 1.5 mAh/cm^2 after 50 cycles. The corresponding volumetric capacity goes down to only 420 mAh/cm^3 .

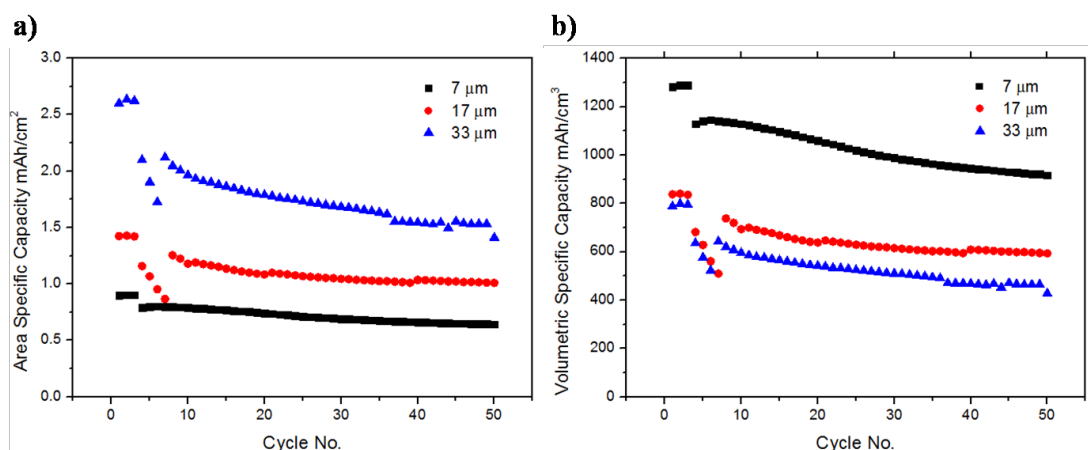


Figure 3. Cycling performance of n-Si/NaCMC/PVA/AB electrodes with different thickness (7 μm, 17 μm and 33 μm): a) Area Specific Capacity vs. Cycle No. and b) Volumetric Specific Capacity vs. Cycle No.

Further, we investigated the symmetric rate capability with the various rates stepwise increased from C/25 to 20 C, as shown in Figure 4. For the thin electrode, it can achieve capacities of 4090, 3990, 3740, 3060, 2500, 2080, 1340, 640, 115 mAh/g at current rates of C/25, C/10, C/5, C/2, 1C, 2C, 5C, 10C and 20 C respectively. The capacity of a thicker electrode varies from 3200 mAh/g to zero at different charge/discharge rates with a dramatic reduce starting from C/2. It is shown in the Figure 4 that the thinner electrode demonstrated a better rate performance than the thick electrode, which is also consistent with our cycling performance results previously. In a non-symmetric rate performance test, we fixed all the lithiation rate at C/25 with delithiation varied from C/25 to 20C. It is shown that both the thin electrode and thick electrode exhibit good performance with a capacity over 2000 mAh/g at 10C, However at 20C, thin electrode gives a capacity above 1000 mAh/g while thick electrode falls down to only 200 mAh/g. With the comparison to the symmetric rate performance previously, it is concluded that lithiation step is perhaps

the performance limited step in our system and thin electrodes always perform better at various C rate.

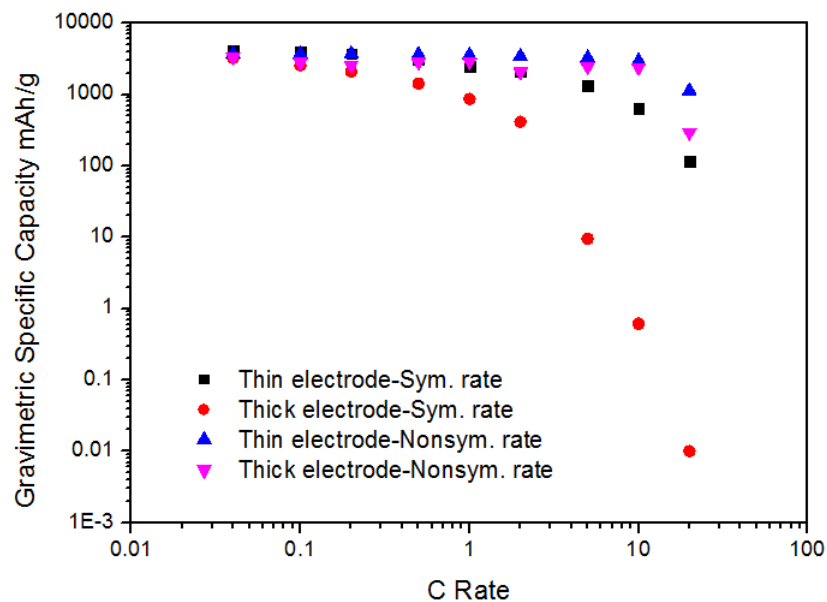


Figure 4. Symmetric and non-symmetric rate performance of thin and thick electrode at different charge/discharge rates from C/25 to 20C. (1C=4.2 A/g)

The cell impedance with different electrode thickness has been taken as shown in Figure 5. Our initial hypothesis was thicker electrode would give a high resistance after long time cycling. However while using a thicker electrode, it turned out to have larger impedance rather than a thinner one. As we considered active area for impedance is not just simply an area of electrode, it should also consider a larger electrode porosity meaning a higher active area. Thus for a thicker electrode, it gave a larger active area than a thinner one, which showed smaller impedance.

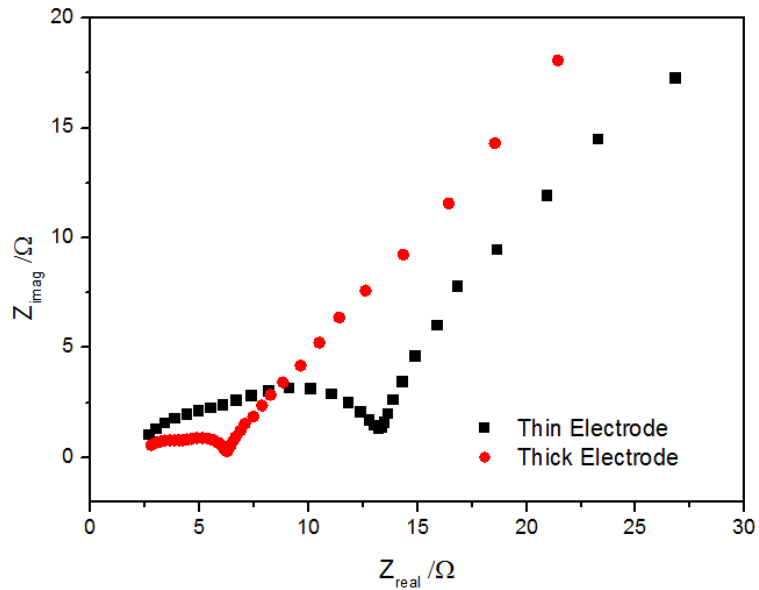


Figure 5. Cell impedance based on two different thickness electrodes. Impedance was recorded after fifty cycles at $C/10$, and the rest were recorded 4 h after half-lithiation in the next cycle.

For a potential application for electric vehicle, the battery will experience at low temperature, depending on the location and seasons of the vehicle being used. Here we study the low temperature cycling performance based on using the n-Si/NaCMC/PVA/AB thin electrode. The electrolyte used in this study is a 1M LiPF_6 in an EC/DEC mixture with an FEC as additive. It is apparently the cell can suffer from a low temperature of 0°C and maintain over 62% capacity about 2000 mAh/g after sixty cycles. However, ongoing research will focus on how to improve a high loading cell operating at moderate high and low temperature condition.

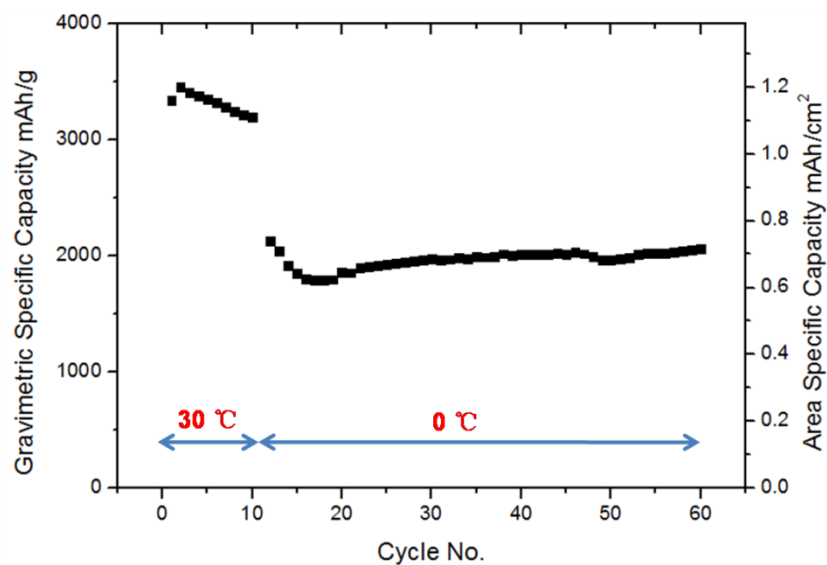


Figure 6. Cycling performance of n-Si/NaCMC/PVA/AB thin electrode at 30 °C (ten cycles) and 0 °C (fifty cycles) at C/10.

Conclusion:

A composite electrode containing nano-sized Si, NaCMC and AB was made with different thickness (7 μm , 17 μm and 33 μm). The fabricated cells all showed a high gravimetric capacity over 2000 mAh/g after 50 cycles as well as a coulombic efficiency of 99 %, which demonstrated that the idea of introducing large surface area nano Si could greatly improve the electrochemical performance of Si-based lithium-ion batteries. Through the study of symmetric and non-symmetric rate test, Si-based lithium ion battery enable to perform a high specific capacity over 1000 mAh/g at 1C charge/discharge either using thin or thick electrode. Considering various thickness of electrodes having different loadings of silicon, the cells performed different level of area capacity and volumetric capacity of Si. It is found that the battery using Si nanoparticles without any structure designing is difficult to

reach a high area capacity, which cannot compete with a conventional battery using graphite. In this report, an area capacity up to 2.5 mAh/cm² is achieved at slow charge/discharge rate using a thicker electrode but fade to 1.5 mA/cm² after 50 cycles at a fast rate. However, volumetric capacity obtained from the same electrode only give a low value of 420 mAh/cm³ when Si loading is high, which is equivalent to the graphite electrode. Through this thickness, rate and cycling study, we aim to set a baseline performance of nano Si as electrodes in lithium-ion batteries and make the information available to research community in this field. The research communities for Si research will need to focus on developing a scalable and low cost nano or micro-sized Si materials¹² and electrode design that can deliver both high stable area capacity and high volumetric capacity at room temperature and low temperature.

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