Conformal Coating of Thin Polymer Electrolyte Layer on Nanostructured Electrode Materials for Three-Dimensional Battery Applications

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ABSTRACT Various three-dimensional (3D) battery architectures have been proposed to address effective power delivery in micro/nanoscale devices and for increasing the stored energy per electrode footprint area. One step toward obtaining 3D configurations in batteries is the formation of core—shell nanowires that combines electrode and electrolyte materials. One of the major challenges however in creating such architectures has been the coating of conformal thin nanolayers of polymer electrolytes around nanostructured electrodes. Here we show conformal coatings of 25—30 nm poly(methyl methacralate) electrolyte layers around individual Ni—Sn nanowires used as anodes for Li ion battery. This configuration shows high discharge capacity and excellent capacity retention even at high rates over extended cycling, allowing for scalable increase in areal capacity with electrode thickness. Our results demonstrate conformal nanoscale anode—electrolyte architectures for an efficient Li ion battery system.

KEYWORDS Li ion battery, 3D battery, nanostructures, conformal coatings

The reversible electrochemistry and the superior gravimetric and volumetric energy storage capacities of lithium ion batteries (LIBs) have propelled them as the dominant power source for a range of portable electronic and vehicular applications.[1−3] But the sluggish rate of charge/discharge remains one of the major challenges plaguing the LIB industry to this day. Current LIBs suffer slow rates of charge/discharge because of (i) slow diffusivity constants of Li ions in most of the electrode materials, (ii) large separator thickness of the order of 20 μm, and (iii) slow electron transport due to large micrometer sized electrode materials. A plethora of recent research efforts have tried addressing these drawbacks of the present day LIBs.[4−10] Shorter Li ion diffusion paths have been achieved by fabricating thin film electrodes.[11] This has led to a significant increase in charge/discharge rates. Yet the thin film technology has the major drawback of possessing lower energy densities. Hence current research is focused on assembling the entire battery (current collectors, anode, solid polymer electrolyte, cathode) in a three-dimensional (3D) nanostructured architecture, and several designs have been proposed.[12] 3D design offers marked improvements in energy and power density especially with respect to the geometric footprint of the device.[12] Efficient means of energy storage with a smaller

areal footprint has been the focus of many researchers in the recent past.[13−20] Hence a redesign from the existing multicomponent assembly to a completely new design of 3D nanoarchitectured electrodes with interpenetrating or conformal assembly[12,21,22] separated by a thin electrolyte/separator will be essential to meet both energy and power requirements.

Nanostructured electrode materials due to their high surface area and superior electronic conductivity can be considered as potential candidates for the construction of 3D batteries.[7,8] A majority of the prior research efforts in 3D designs have been limited to the microstructured (∼40 μm pore size) battery architecture.[13,18] Among the several methods available for synthesis of nanowire electrodes, template-assisted synthesis has been shown to be a simple and versatile technique with excellent control over nanowire dimensions.[23,24] Conformal coating of electrode materials around nanostructured current collectors pioneered by Simon and co-workers[4,25] has shown fast rates of charge and discharge maintaining high energy densities. However, achieving uniform coatings of separator/electrolyte units around nanostructured electrode materials has been challenging, and the reports addressing the same are limited.[26,27] One method which is gaining focus is the self-limiting electrodeposition of nonconducting polymers such as poly(phenylene oxide) (PPO) around nanostructured electrodes.[26,27] The above method of coating polymers by electrodeposition requires extremely inert conditions to attain reliable conformal coatings around the electrode material. The other simple, established technique of coating polymer layers
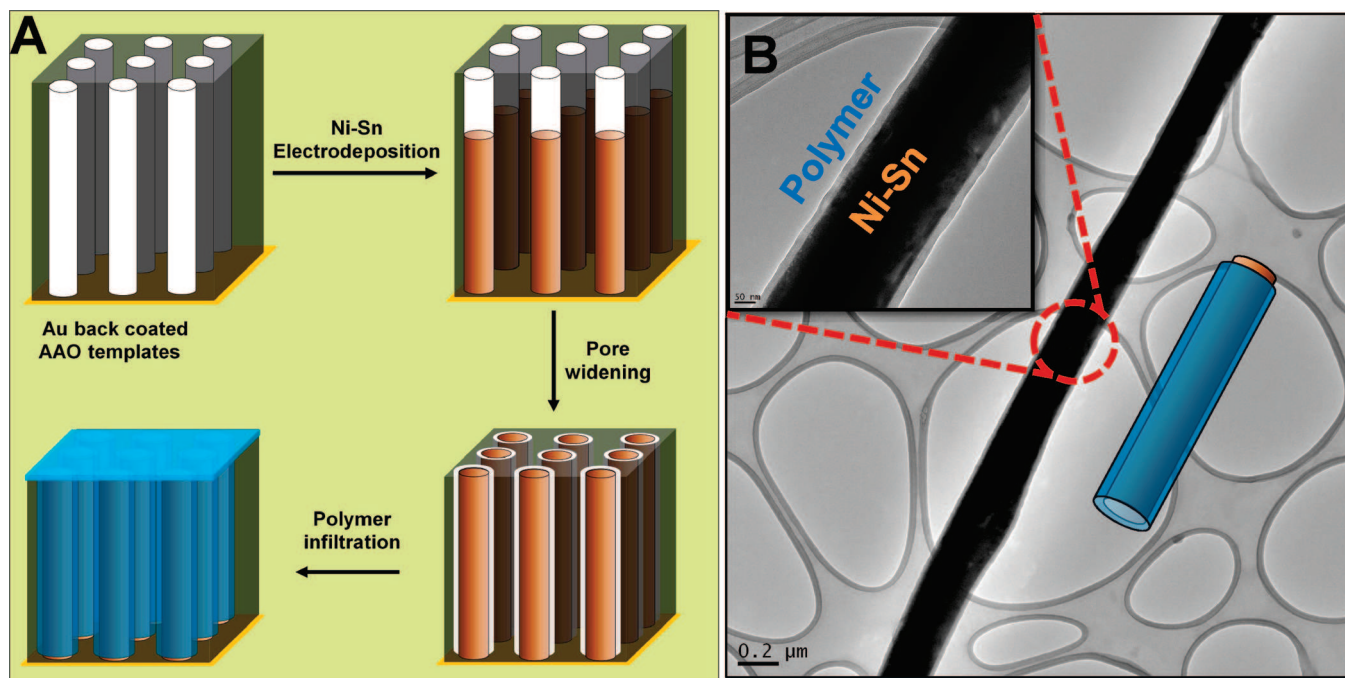
FIGURE 1. Fabrication of nanostructured conformal Ni−Sn/PMMA hybrid assembly. (A) Schematic showing the fabrication of the novel nanostructured conformal configuration of the electrode/separator assembly. Drop coating of PMMA layer onto the pore-widened alumina template results in 3D conformal configuration. (B) TEM image of the conformal configuration showing the conformal PMMA layer (~25 nm) around a ~3 μm long segment of a Ni−Sn nanowire. The high-resolution image (inset) clearly shows a good interface between the thin PMMA layer around the Ni−Sn nanowire. A schematic of single conformal Ni−Sn/PMMA nanowire assembly is also shown.

on electrode materials is by spin/drop coating.[28,29] Such polymer coatings not only serve as the separator/electrolyte functionality but also could help in controlling and forming stable solid electrolyte interphase (SEI) film formation on the high surface area nanostructured electrodes.[30−32] SEI film formation and stability influence irreversible capacity loss and cycling characteristics of Li ion battery electrodes.[30,33] The use of appropriate electrolyte for the active material, carbon coatings/composites, and surface modification of electrode have included some of the efforts to address this issue.[30,34−36] Hence there exists a need for innovative approaches to control the SEI formation on high volume expansion intermetallic[37,38] based electrode materials. Herein we report the fabrication of a conformal layer of ~25 nm thick poly(methyl methacralate) (PMMA) (separator/gel electrolyte) around an individual nanostructured electrode (Ni−Sn intermetallic nanowire) using a hard template assisted drop coating technique. The nanostructured conformal configuration of the gel electrolyte has led to improved rate capabilities and discharge capacities of the electrode per footprint area (footprint area: overall device area) compared to its planar (stacked layers as used in bulk technologies) counterpart.

Owing to its high specific capacity, low cost and easy fabrication, Ni−Sn intermetallic nanowires have been chosen as the prototype electrode material.[39] Ni−Sn nanowires were grown inside pores of an anodized alumina template using a galvanostatic electrodeposition method (see the materials and methods section and Figures S1 and S2 in the Supporting Information). Spin coating or drop coating fol-

lowed by wiping the excess solution on the surface of the template was used to coat a thin layer of PMMA onto the Ni−Sn electrode for the planar and conformal configuration, respectively. Using a combination of the above two techniques to grow nanostructured electrode and electrolyte/separator materials in the alumina template, the conformal configuration has been realized for the electrode−electrolyte assembly (Figure 1A). Electron microscopy images of the conformal configurations show the well-developed interfaces between the electrode and the polymer electrolyte/separator (Figure 1B). An entire nanowire was visualized at 24 continuous segments by TEM to confirm the conformal nature of the coating along the length of the nanowire as shown in Figure S3 (Supporting Information). The conformal nature of the PMMA coating around the nanowires was observed for all the Ni−Sn nanowires imaged using TEM. The conformal configuration results in a core−shell nanostructure and has much higher interfacial area compared to the conventional planar configuration. This leads to an electrode volume gain and allows for direct access of Li ions to the entire surface of the cylindrical nanowires. But in the case of the planar configuration Li ion transport occurs only across the planar interface between the electrode and electrolyte. Hence the conformal configuration of electrode−electrolyte assembly is expected to exhibit superior electrochemical properties compared to the respective planar thin film based configuration.

Ni−Sn/PMMA electrode−electrolyte assemblies with planar and conformal nanostructured configurations were tested
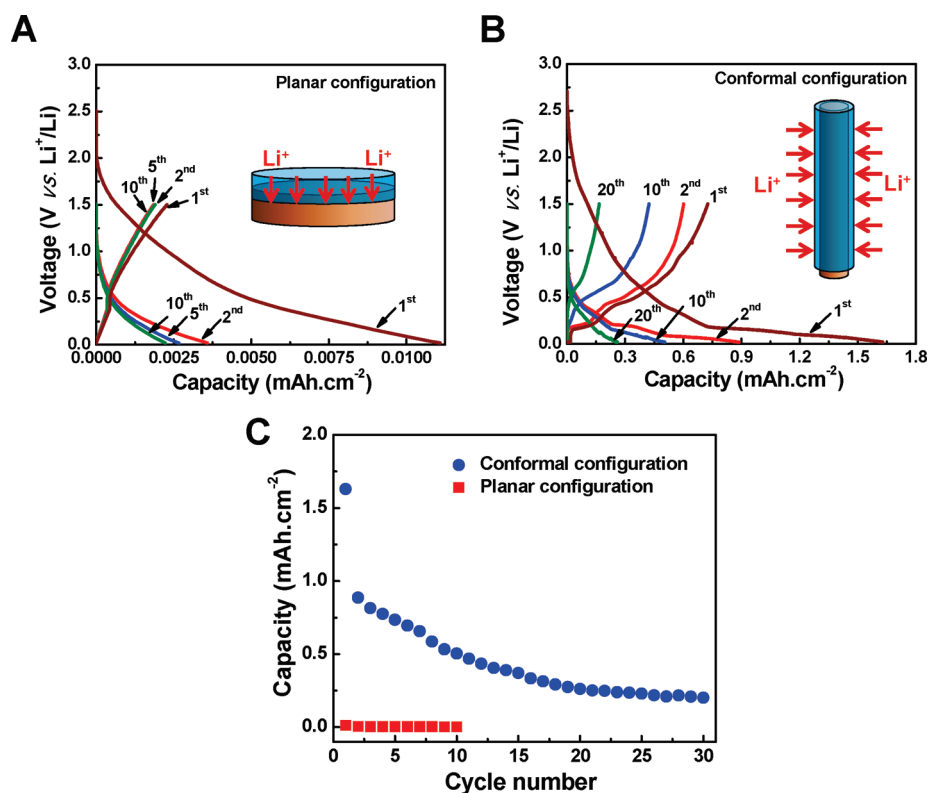
FIGURE 2. Electrochemical performance of Ni−Sn/PMMA assembly in planar and conformal configurations, galvanostatically cycled in Li-half cells. (A) Variation in voltage vs capacity per footprint area for the planar Ni−Sn/PMMA electrode/electrolyte configuration cycled at a rate of 0.12 mA/cm² between 1.5 and 0.02 V vs Li/Li⁺ using PMMA separator soaked in 1 M solution of LiPF$_6$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. (Inset: Schematic of planar configuration with the arrows indicating direction of Li ion transport.) (B) Variation in voltage vs capacity per footprint area for the conformal Ni−Sn/PMMA electrode/electrolyte configuration cycled at a rate of 0.12 mA/cm² between 1.5 and 0.02 V vs Li/Li⁺ using PMMA separator soaked in 1 M solution of LiPF$_6$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. (Inset: Schematic of the core−shell morphology of individual nanowires in the conformal configuration with the radial direction of Li ion transport.) (C) Comparison of the cycling behavior of the planar and conformal configuration. The conformal configuration showed a reversible capacity of 0.26 mAh/cm² after 30 cycles of charge/discharge which was 2 orders of magnitude greater than the capacity delivered by the planar design.

for their electrochemical performance in Li half cells by galvanostatic charge/discharge cycling between 1.5 and 0.02 V vs Li/Li⁺, with Ni−Sn as the working electrode. The conformal PMMA layer soaked in liquid electrolyte solution formed the gel electrolyte and separator. For the conformal nanostructured electrode−electrolyte configuration, nanowires of height 10 μm were electrodeposited in the AAO templates and for the planar configuration a film of same thickness was electrodeposited on a copper foil. The potential vs capacity curves for the two electrode−electrolyte configurations (Figure 2) at a current rate of 0.12 mA/cm² show typical Li insertion/extraction behavior of tin-based intermetallic anodes. Li ion transport in these configurations has been schematically illustrated in the respective plots. It can be clearly seen that the capacity per unit area of the conformal configuration is higher than that for the planar counterpart. The thin film based planar configuration showed a reversible capacity of ~0.002 mAh/cm² after 10 cycles of charge/discharge whereas the conformal configuration was able to retain a reversible capacity of ~0.26 mAh/cm² even after 30 cycles of charge/discharge. The novel conformal nanostructured electrode−electrolyte configuration shows

an improvement in the reversible capacity by 2 orders of magnitude. Moving to the third dimension with a conformal nanowire based configuration has resulted in geometrical area gain and an associated electrode volume gain. This leads to shorter transport path for Li ion diffusion between the electrodes. On the contrary in the planar configuration, the Li ions diffuse through the entire length of the nanowire or the bulk film, respectively. The slow transport of Li ions through solid state anode materials leads to the development of a concentration polarization which results in a large loss in capacity delivered.[40] In the case of the conformal configuration, the problem of concentration polarization is reduced significantly by the conformal wrapping of PMMA electrolyte around every individual nanowire electrode hence resulting in short radial Li ion diffusion distances. Hence the galvanostatic cycling results (Figure 2C) clearly delineate that the conformal design of the electrode−electrolyte assembly in LIB leads to efficient performance with good cycling characteristics and energy densities compared to conventional planar design.

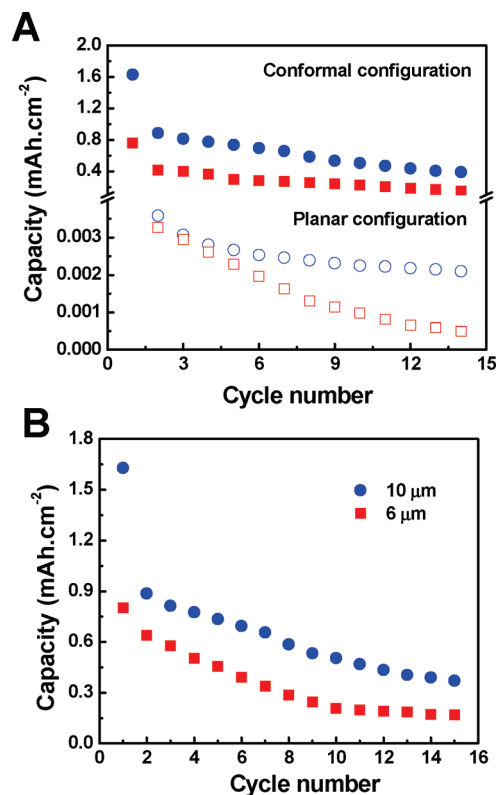To realize the high rate power capabilities of this novel conformal electrode−electrolyte assembly for 3D nano/

FIGURE 3. Rate capability and capacity retention of conformal Ni−Sn/PMMA assembly. (A) Comparison of rate capability of the planar and conformal configuration. Blue solid circle and red solid square symbols correspond to the conformal configuration cycled at 0.12 and 0.3 mA/cm^2 respectively. Blue open circle and red open square correspond to the planar configuration cycled at 0.12 and 0.3 mA/cm^2, respectively. (B) Comparison of cycling behavior of Ni−Sn/PMMA core/shell nanowire with different lengths of the Ni−Sn nanowire. Reversible capacities of ∼0.4 mAh/cm^2 (10 μm Ni−Sn) and ∼0.2 mAh/cm^2 (6 μm Ni−Sn) were observed after 15 cycles of charge/discharge.

microbattery applications, we studied its electrochemical performance at higher current rates and with increasing heights of electrode segments, maintaining the areal footprint. Ni−Sn/PMMA (gel electrolyte) with conformal configuration and electrode length of ∼10 μm was galvanostatically cycled in a Li half-cell at different current rates of 0.12 mA/cm^2 (0.5C) and 0.3 mA/cm^2 (3C) (Figure 3A) (C rate is defined as the rate at which the nominal capacity of the electrode material is achieved: 1C, 1 h to discharge the nominal capacity of the cell). A planar electrode−electrolyte assembly with same electrode height (thickness) is also tested for comparison. The difference in the initial capacity could be due to the differences in the accessibility of the bulk electrode film. The capacity behavior of planar assembly follows a typical thin film electrode with a constant decrease at higher current rates. Excellent rate capability is observed with the conformal design and shows good capacity retention even at higher current rates. Reversible and steady capacity of 0.15 mAh/cm^2 was achieved at a high current rate of 0.3 mA/cm^2. This can be attributed to the short

diffusion distance in the Ni−Sn nanowire due to radial diffusion of Li ions.

There are other advantages of the conformal design, apart from the high rate capability, compared to its planar counterpart. Thin film batteries suffer from low energy densities while achieving faster Li ion kinetics in the battery. Increase in film thickness leads to loss in rate capability and the discharge capacity due to the development of concentration polarization in the electrode.[40] It results in huge Ohmic losses and transport resistances. This problem can be smartly alleviated by the conformal design of electrolyte around the electrode which allows for the growth of longer nanowires ensuring the conformal coating of the entire nanowire with the polymer separator, without sacrificing the small footprint area. Short Li ion distances along the entire length of the nanowire leads to the efficient utilization of the nanowire's capacity. A comparison of the theoretical capacity expected (based on theoretical specific capacity of Ni−Sn electrode) and the actual measured initial capacity helps us find the electrode utilization for the planar and conformal configurations. Using the theoretical specific capacity of Ni−Sn electrode (∼730 mAh/g[12]) and the estimated electrode masses for the two electrode configurations (planar, ∼4.2 mg; conformal, ∼1 mg) we can obtain the theoretically expected capacities to be 3.06 and 0.73 mAh for the planar and conformal configurations, respectively (for details see Supporting Information). On comparing these theoretical capacity values to the measured electrochemical values of the initial capacities (Figure 2C) of the electrode configurations, we find a very good match in the case of the conformal configuration for the first cycle (∼0.78 mAh at current rate 0.12 mA/cm^2 (0.5C)) (within reasonable error in mass measurement) which implies far better utilization of the electrode material than that of the planar configuration which showed an initial capacity ∼0.02 mAh/cm^2 at the same current rate. The capacity losses observed in the subsequent cycles for the conformal design are characteristic losses due to large volume expansion and loss in electrode crystallinity, observed in tin based electrode materials.[33] Contrastingly in the case of the planar configuration (Figure 2C) we observe that even the initial capacities fall far behind the theoretically predicted values (see Supporting Information) indicating poor utilization of electrode material. This discrepancy in the measured and theoretical initial capacities for the 2D configuration is attributed to the severe concentration polarization effects which occur as a result of longer diffusion lengths in the planar films as the film thickness is increased.[40] Hence an increase in the height of the electrode segment, with the same small footprint area, is expected to result in increased areal capacity along with high power capabilities.[12] To carry out this study, two samples of Ni−Sn/PMMA core−shell nanowires with varying heights of 6 and 10 μm were galvanostatically cycled in Li half-cells at current rates of 0.06 and 0.12 mA/cm^2, respectively. The capacity vs cycle number plot (Figure 3B) clearly shows the increase in areal
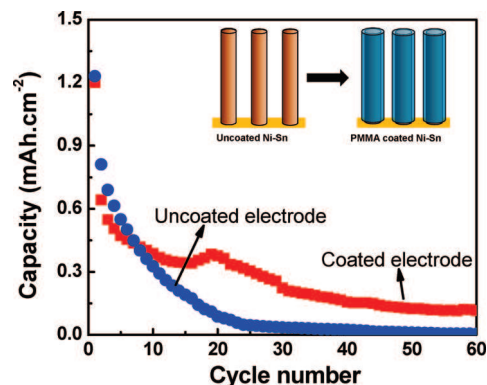
FIGURE 4. Electrochemical performance of conformally coated (PMMA) Ni–Sn nanowires and uncoated Ni–Sn nanowires. Blue solid circles and red solid square symbols correspond to the cycling characteristics of 3D PMMA coated Ni–Sn nanowires and the uncoated Ni–Sn nanowires (nanowire length ∼12 μm) cycled at 0.3 mA/cm^2 (3C), respectively. The PMMA coating soaked in 1 M solution of LiPF$_6$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) served as the separator/electrolyte unit for conformal PMMA coated Ni–Sn nanowires whereas an external glass microfiber separator in 1 M solution of LiPF$_6$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as a separator for the uncoated Ni–Sn nanowires. A schematic of the uncoated and PMMA coated Ni–Sn nanowires is shown in the Inset.

capacity with increasing electrode height. Reversible capacities of 0.17 and 0.37 mAh/cm^2 have been obtained for samples with Ni–Sn height of 6 and 10 μm, respectively. This further confirms the conformal nature of the polymer coatings around the entire length of the nanowire electrode, as there is no change in the Li ion transport distance. The discharge profiles of the two samples show that fast Li ion kinetics (power capability) is retained even after increasing the height of the Ni–Sn nanowire electrodes (see Figures S4 and S5 in the Supporting Information). In general, Sn based electrodes suffer from capacity decay with cycling;[33,39] however, our present study intends to demonstrate the novel conformal configuration of the electrode–electrolyte assembly for 3D nano/microbattery applications and the concept can be extended for other electrode systems as well. Using Li half-cell measurements, we clearly show that the conformal design of the electrode–electrolyte assembly brings an innovative approach to improving areal energy densities of low dimensional batteries yet maintaining their high power capabilities.

We have conducted control experiments to compare the electrochemical performance between PMMA coated and uncoated Ni–Sn nanowires. Galvanostatic charge/discharge measurements were conducted on coated and uncoated nanowire arrays at a current rate of 0.3 mA/cm^2 (3C) to investigate the rate capability of the two configurations. From the galvanostatic cycling results (Figure 4) it is clear that the PMMA coated Ni–Sn nanowires show an improvement in the reversible capacity retention at a high current rate of 3C. Conformally coated Ni–Sn nanowires show a stable reversible capacity of ∼0.2 mAh/cm^2 for

galvanostatic cycling at fast rates of charge/discharge (3C) up to 60 cycles of charge/discharge. From these results we believe that the conformal PMMA coating could be playing a role in improvement of rate capability of the Ni–Sn nanowires. The presence of an interfacial reaction between Ni–Sn and the liquid electrolyte leads to the formation of the SEI film on the electrode surface leading to capacity loss over cycling.[38] Recent research efforts have characterized the surface films on intermetallic anodes specifically Ni–Sn based anodes and have discussed the dependence of cycling characteristics on surface reactions.[37,38] Herein, we speculate that the polymer coating around the Ni–Sn nanowires could be helping in stabilizing the SEI film and conceivably suppressing the detrimental surface effects on the electrode leading to the improved cycling characteristics. The exact details of the SEI formation mechanisms and its evolution over cycling are yet to be probed and understood. We believe that the coating of polymers (which also serves as the separator functionality) around individual electrode Ni–Sn nanowires could open a new direction of research toward improving cycling characteristics of this high volume expansion electrode material without the need of external surface modifications.[30] More in-depth studies are underway to understand the direct relation between polymer coatings around high volume expansion electrode nanowires and capacity fade characteristics. Various other polymer/electrode systems need to be investigated to understand the exact nature of polymer/electrode interface evolution over extended cycling. We have conducted extensive TEM analysis of the conformally coated Ni–Sn nanowires after galvanostatic charge/discharge cycling which also reveals that the PMMA shell is intact around the Ni–Sn nanowires. (See Figure S6 in the Supporting Information.) The absence of pinholes even after extended cycling at a high current rate (3C) clearly demonstrates the strength of the electrode–electrolyte interface. Hence the polymer-coated electrode nanowires could serve as a great candidate for future 3D lithium ion batteries.

To conclude, we have demonstrated a simple template assisted technique to fabricate nanoarchitectured conformal electrode/electrolyte assembly which can be useful in Li ion nano/microbattery systems. A thin conformal layer of PMMA deposited around the Ni–Sn nanowire electrode provides the separator functionality to the assembly and serves as the gel electrolyte when soaked with liquid electrolyte. The conformal configuration showed excellent electrochemical performance with 2 orders of magnitude improvement in the reversible discharge capacities, compared to its planar counterpart. High rate capability over extended cycling resulting from the nanoarchitectured conformal electrode–electrolyte assembly has also been demonstrated. The PMMA coating has been observed to stay intact around the Ni–Sn nanowires over extended cycling at high current rates and

has been shown to improve the cycling characteristics of the bare nanowires. We believe that our simple approach could easily be extended to deposit other active electrode materials and polymer separators which could lead to the development of an efficient nanoscale Li ion battery. The conformal configuration of the PMMA coated electrode we have shown here is an important step toward realizing the true 3D nanostructured battery where the anode, electrolyte, and cathode are all conformally integrated into the single nanowire assembly.

Supporting Information Available. Details of the materials and methods used. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Armand, M.; Tarascon, J. M. *Nature* **2008**, *451*, 652–657.

(2) Whittingham, M. S. *Chem. Rev.* **2004**, *104*, 4271–4301.

(3) Van Schalkwijk, W.; Scrosati, B. *Advances in Lithium-Ion Batteries*; Kluwer Academic/Plenum: New York, 2002.

(4) Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M. *Nat. Mater.* **2006**, *5*, 567–573.

(5) Chung, S. Y.; Bloking, J. T.; Chiang, Y. M. *Nat. Mater.* **2002**, *1*, 123–128.

(6) Li, N.; Martin, C. R.; Scrosati, B. *Electrochem. Solid-State Lett.* **2000**, *3*, 316–318.

(7) Aricò, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Van Schalkwijk, W. *Nat. Mater.* **2005**, *4*, 366–377.

(8) Reddy, A. L. M.; Shaijumon, M. M.; Gowda, S. R.; Ajayan, P. M. *Nano Lett.* **2009**, *9*, 1002–1006.

(9) Endo, M.; Kim, C.; Nishimura, K.; Fujino, T.; Miyashita, K. *Carbon* **1999**, *38*, 183–197.

(10) Lee, S.-H.; Kim, Y.-H.; Deshpande, R.; Parilla, P. A.; Whitney, E.; Gillaspie, D. T.; Jones, K. M.; Mahan, A. H.; Zhang, S.; Dillon, A. C. *Adv. Mater.* **2008**, *20*, 3627–3632.

(11) Bates, J. B.; Dudney, N. J.; Neudecker, B.; Ueda, A.; Evans, C. D. *Solid State Ionics* **1999**, *135*, 33–45.

(12) Long, J. W.; Dunn, B.; Rolison, D. R.; White, H. S. *Chem. Rev.* **2004**, *104*, 4463–4492.

(13) Golodnitsky, D.; Nathan, M.; Yufit, V.; Strauss, E.; Freedman, K.; Burstein, L.; Gladkich, A.; Peled, E. *Solid State Ionics* **2006**, *177*, 26–32.

(14) Hassoun, J.; Panero, S.; Simon, P.; Taberna, P. L.; Scrosati, B. *Adv. Mater.* **2007**, *19*, 1632–1635.

(15) Nam, K. T.; Kim, D.-W.; Yoo, P. J.; Chiang, Y. -C.; Meethong, N.; Hammond, P. T.; Chiang, Y. -M.; Belcher, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 17227–17231.

(16) Shaijumon, M. M.; Ou, F. S.; Ci, L.; Ajayan, P. M. *Chem. Commun.* **2008**, *20*, 2373–2375.

(17) Powers, R. A. *Proc. IEEE* **1995**, *83*, 687–693.

(18) Nathan, M.; Golodnitsky, D.; Yufit, V.; Strauss, E.; Ripenbein, T.; Shechtman, I.; Menkin, S.; Peled, E. *J. Microelectromech. Syst.* **2005**, *14*, 879–885.

(19) Cho, Y. K.; Wartena, R.; Tobias, S. M.; Chiang, Y. -M. *Adv. Funct. Mater.* **2010**, *17*, 379–389.

(20) Dillon, A. C.; Mahan, A. H.; Deshpande, R.; Parilla, P. A.; Jones, K. M.; Lee, S. H. *Thin Solid Films* **2008**, *516*, 794–497.

(21) Cheah, S. K.; Perre, E.; Rooth, M.; Fondell, M.; Harsta, A.; Nyholm, L.; Boman, M.; Gustaffson, T.; Lu, J.; Simon, P.; Edstrom, K. *Nano Lett.* **2009**, *9*, 3230–3233.

(22) Madou, M. J.; Jornet, F. G. US Patent 11837286, 2007.

(23) Hurst, S. J.; Payne, E. K.; Qin, L.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2672–2692.

(24) Cheng, F.; Tao, Z.; Liang, J.; Chen, J. *Chem. Mater.* **2007**, *20*, 667–681.

(25) Bazin, L.; Mitra, S.; Taberna, P. L.; Poizot, P.; Gressier, M.; Menu, M. J.; Barnabe, A.; Simon, P.; Tarascon, J. -M. *J. Power Sources* **2009**, *188*, 578–582.

(26) Long, J. W.; Rhodes, C. P.; Young, A. L.; Rolison, D. R. *Nano Lett.* **2003**, *3*, 1151–1161.

(27) Rhodes, C. P.; Long, J. W.; Doescher, M. S.; Fontanella, J. J.; Rolison, D. R. *J. Phys. Chem. B* **2004**, *108*, 13079–13087.

(28) Dewan, C.; Teeters, D. *J. Power Sources* **2003**, *119*, 310–315.

(29) Pushparaj, V. L.; Shaijumon, M. M.; Kumar, A.; Murugesan, S.; Ci, L.; Vajtai, R.; Linhardt, R. J.; Nalamasu, O.; Ajayan, P. M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 13574–13577.

(30) Fu, L. J.; Liu, H.; Li, C.; Wu, Y. P.; Rahm, E.; Holze, R.; Wu, H. Q. *Solid State Sci.* **2006**, *8*, 113–128.

(31) Balbuna, P. B.; Wang, Y. *Lithium-Ion Batteries: Solid-Electrolyte Interphase*; Imperial College Press: London, 2004.

(32) Guo, K.; Pan, Q.; Fang, S. *J. Power Sources* **1997**, *68*, 87–90.

(33) Winter, M.; Besenhard, J. O. *Electrochim. Acta* **1999**, *45*, 31–50.

(34) Ulus, A.; Rosenberg, Y.; Burstein, L.; Peled, E. *J. Electrochem. Soc.* **2002**, *149*, A635–A643.

(35) Kim, T.-J.; Son, D.; Cho, J.; Park, B.; Yang, H. *Electrochim. Acta* **2004**, *49*, 4405–4410.

(36) Lee, K. T.; Jung, Y. S.; Oh, S. M. *J. Am. Chem. Soc.* **2003**, *125*, 5652–5653.

(37) Stjerndahl, M.; Bryngelsson, H.; Gustafsson, T.; Vaughey, J. T.; Thackeray, M. M.; Edstrom, K. *Electrochim. Acta* **2007**, *52*, 4947–4955.

(38) Ehinon, K. K. D.; Naille, S.; Dedryvère, R.; Lippens, P.-E.; Jumas, J.-C.; Gonbeau, D. *Chem. Mater.* **2008**, *20*, 5388–5398.

(39) Hassoun, J.; Panero, S.; Scrosati, B. *J Power Sources* **2006**, *160*, 1336–134.

(40) Owen, J. R. *Chem. Soc. Rev.* **1997**, *26*, 259–267.