

## **Pouch-cell architecture downscaled to coin cells for electrochemical characterization of bilateral electrodes**

Dan Schneier<sup>1</sup>, Nimrod Harpak<sup>1</sup>, Fernando Patolsky<sup>1,2</sup>, Diana Golodnitsky<sup>1,3</sup>, Emanuel Peled<sup>1</sup>

1-School of Chemistry, Faculty of Exact Sciences; Tel Aviv University, Tel Aviv, 6997801, Israel.

2-Department of Materials Science and Engineering, the Iby and Aladar Fleischman Faculty of Engineering; Tel Aviv University, Tel Aviv, 6997801, Israel.

3-Applied Materials Research Center, Tel Aviv University, Tel Aviv, 6997801, Israel.

*Emails: [peled@tauex.tau.ac.il](mailto:peled@tauex.tau.ac.il)*

### **Abstract**

Research groups all over the world test new innovative electrodes for batteries aimed to be the next generation of energy storage devices. The most common and efficient tool for testing these electrodes is the lab-scale coin cell, which houses two 1-sided electrodes. However, many new electrodes in development are bilateral by design, adapted for use in pouch or rolled cells. In addition, quite often new electrodes, such as silicon and sulfur based, are able to hold large areal capacities that might not be properly tested with any single counter electrode. Here we suggest a new technique to assemble coin cells that allows the use of two unilateral electrodes with a bilateral electrode sandwiched between them. This method requires no unique tools or materials, and can help labs with limited resources test their electrodes in more realistic, pouch type conditions that can better showcase the capabilities of their novel research products.

### **Body of text**

Lithium ion batteries are presently still the most popular choice for portable energy storage devices, with intercalation and conversion chemistry that has not changed drastically since its first commercialization 30 years ago[1]. With that being said, new technologies are developed all around the world aiming to break through as the next generation of battery materials and configurations[2,3]. While The common coin cell is still the preferred tool for electrochemical testing of new electrode materials[4–6], better characterization of batteries for practical applications requires new ideas of how to modify cells to provide more relevant and detailed results. Coin and Swagelok cells can be fitted with a reference electrode to differentiate the processes on the working and counter electrodes[7–9]. Cells can also be modified to allow for in-situ characterization by methods such as SIMS[10], NMR[11] or AFM[12].

New materials and synthesis methods are another crucial part of the advancement process of LIBs. In addition to the production of new active materials that are integrated in existing technologies, some groups suggest preparation of whole, high active-material loading electrodes using various

methods. Leveau et al. fabricated silicon nano-trees by chemical vapor deposition with  $2.5\text{mgSi}/\text{cm}^2$ [13]. Wang et al also created a binder-free silicon based electrode by electrospinning a silicon/carbon composite with over  $2\text{mgSi}/\text{cm}^2$ [14]. On the cathode development front, Yang et al. impregnated carbon papers with  $\text{CoS}_3$  and achieved sulfur loadings of  $10\text{mgS}/\text{cm}^2$ [15] and Yuan et al. fabricated sulfur-based cathodes by filtration of sulfur/carbon nanotubes suspensions with up to  $17.3\text{mgS}/\text{cm}^2$ [16].

These technologies that are being developed need to be electrochemically characterized in half cells first (versus lithium counter electrodes) as well as in full cells, versus commercial counter electrodes that showcase the new electrodes' true applicability. To that end the electrodes should be tested in lab scaled cells as efficiently as possible before testing them in larger cells such as jellyroll batteries and pouch cells[1]. This issue could be challenging with bilateral electrodes since concentration gradients could form in the electrodes' structure[17] that are different between single sided and bilateral cells. High loading electrodes will also be a challenge in that counter electrodes may not be available to provide a well-balanced cell[18]. Most of the abovementioned methods produce electrodes smaller than A4 papers, so conservation of materials may also be a crucial factor.

For these reasons, we propose a simple method to assemble coin cells in an architecture which simulates pouch cells without any special equipment or devices needed. This method is presented here for 2032 cells in the configuration of cathode/anode/cathode but could be used in the reverse order for cathode research.

In order to assemble a bilateral cell, one only needs two additional separators beyond conventional coin cells, a thin copper strip to connect the anode to the current collector and an Al strip to connect the cathodes. These metal strips should be about 0.2cm by 1.8cm, and any standard electrode current collector will do. The scheme of the cell is presented in Figure 1. Before assembly of the cell the only recommended step is to reduce the size of two separators by about 2-3mm from one side, as shown in the figure. For the assembly of 2032 cells we recommend electrodes 12mm in diameter, although other sizes may also be usable. The steps of assembly are as follows:

- a. Place the 1.8cm long Al strip in the cell base beneath the SS disc and press it to the side of the base.
- b. Place a 12 mm wide cathode, active surface facing upwards, and a 19 mm wide separator on it.
- c. Place the 1.8cm long Cu strip on the separator at the opposite direction from the Al foil, and the 12mm wide anode on top of it.
- d. Place a cut 19mm wide separator on the anode with the straight, cut side of the separator facing towards the Cu strip.
- e. Place the second 12mm wide cathode at the center of the stack, active surface facing down. Fold the Al strip down to rest on the back of the cathode.
- f. Place the third 19mm wide separator at the same position as the second, and fold down the Cu strip. It is important at this point to make sure that the Cu strip is folded as close as

possible to the cut line of the separators, so that the strip goes “inside” the cell gasket. Lay the SS disc on the folded Cu strip.

- g. Add electrolyte, the gasket, the spring, the lid and seal the cell.

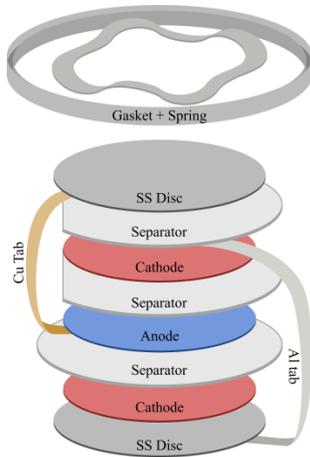


Figure 1- a scheme of the coin cell with a bilateral anode and two cathodes

As proof of the efficiency of this configuration we have tested cells with silicon nanowire anodes (SiNWs) grown on a stainless steel mesh[19]. These anodes are grown in a single step chemical vapor deposition process and as such are by default bilateral. SEM images in Figure 2 show planar and cross-sectional views of these SiNWs electrodes. Thanks to their high surface area silicon loadings of  $1\text{-}5\text{mg}/\text{cm}^2$  have been demonstrated, with capacities of up to  $15\text{mAh}/\text{cm}^2$  and  $3000\text{mAh}/\text{gSi}$ [20]. For these anodes regular unilateral commercial cathodes would not be able to provide the capacity required to test a well-balanced cell, so a pouch-like cell would be optimal for small scale tests of these anodes. On the other hand, lab-scale synthesis processes often produce limited amounts of materials which must be carefully utilized, and actual pouch cells can be wasteful and they require different assembly equipment.

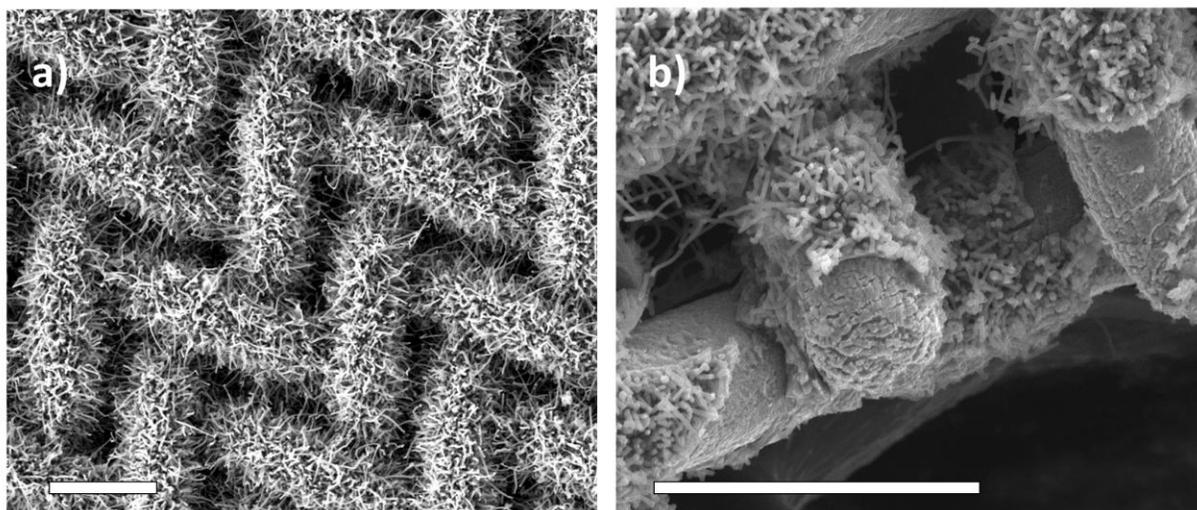


Figure 2- SEM images of the bilateral SiNWs anodes, a) planar view, b) cross section of the edge, bar-50 $\mu\text{m}$

For these reasons a coin cell configuration with a “pouch-like” stack could be beneficial. The cycle life of a cell with such an anode, containing approximately  $2.7\text{mgSi}/\text{cm}^2$ , is demonstrated in Figure 3. Before assembly the anode was coated on one side with a drop of carbon nanotube suspension (TUBALL BATT, OCSiAl) for the sake of better electrical conductivity between the stainless steel substrate of the anode and the Cu strip. The anode is sandwiched between two commercial NMC 622 cathodes (Targray) with a reversible capacity of approximately  $2\text{mAh}/\text{cm}^2$  each. The cell was tested at 2.8-4.1V, displaying capacities of  $1200\text{mAh}/\text{gSi}$  at C/3 and  $800\text{mAh}/\text{gSi}$  at 1C. The cell presented a capacity fade rate of 0.3%/cycle at 1C. The common practice of pairing the anode with a single cathode limits the anode’s practical capacity that can reach up to  $8\text{mAh}/\text{cm}^2$ . Our design results in a well-balanced cell. Our cells provide over 3 times the gravimetric capacity ( $\sim 1200\text{mAh}/\text{grSi}$ ) of commercial graphite anodes[1]. Given that, we prevent lithium deposition on the anode by still ensuring anodic excess. It displayed initial geometric capacity of  $3.8/2 = 1.9\text{mAh}/\text{cm}^2$ , using most of the cathodes’ theoretical capacity of  $2\text{mAh}/\text{cm}^2$  each. The performance of the cell when charged at 1C rates even surpasses that of the 1/AAA jellyroll cells presented in our previous works (ref [20]), with  $2.7\text{mAh}/\text{cm}^2$  in the coin cell versus  $2.5\text{mAh}/\text{cm}^2$  in the 1/AAA cell.

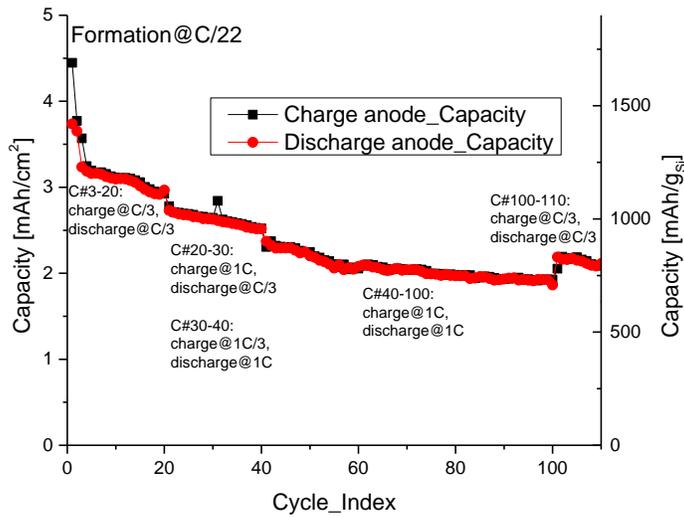


Figure 3- cycle life of a coin cell with a bilateral SiNWs anode and two NMC cathodes, cycled at 2.8-4.1V

Electrochemical impedance spectroscopy (EIS) is a convenient in-operando method for evaluation of the impedance components in the cell at various point of its cycle life. We present in Figure 4 EIS spectra of the cell after 100 cycles, after charge and discharge. The intercept of the first semicircle with the X axis, which represents the resistance of the electrolyte of the cell ( $R_{\text{bulk}}$ ), is 2 ohm , close to the  $R_{\text{bulk}}$  in regular coin cells using the same SiNWs anode is [20]. This proves that the unique connections of the electrodes do not hinder the current flow into and out of the electrodes. The diameter of the semi-circles represents the sum of charge transfer resistances in SiNW anode and NMC cathode. The higher resistance of the electrodes in the discharged state can be attributed to the hindered charge transfer process in the lithiated cathode [21].

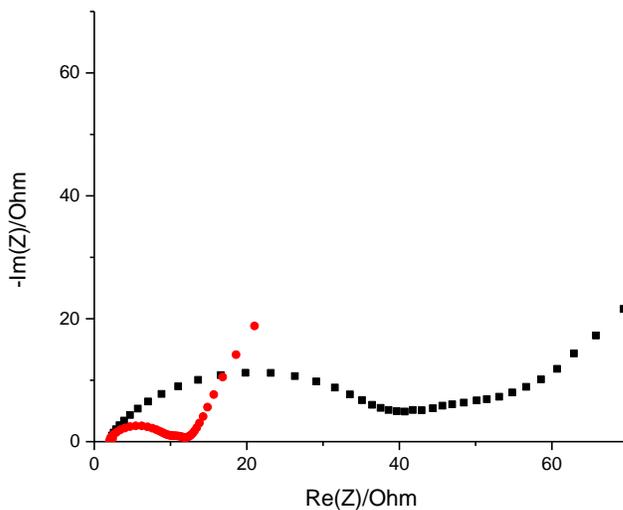


Figure 4- EIS spectra of the bilateral cell at cycle 100 (red- after charge, blue- after discharge)

In summary, we have developed a simple method of coin cell assembly for the characterization of electrochemical performance of bilateral electrodes. The use of this method is exemplified with CVD-grown SiNWs anodes encased between two commercial cathodes. We believe that the simplicity of this architecture will allow other materials to be tested just as efficiently. This method allows developers of battery electrodes to test their products in a manner that preserves materials and equipment while maintaining performances similar to larger scale jellyroll and pouch cells.

- [1] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, 414 (2001) 359–367.
- [2] G.E. Blomgren, J.E. Soc, G.E. Blomgren, The Development and Future of Lithium Ion Batteries The Development and Future of Lithium Ion Batteries, (2017). doi:10.1149/2.0251701jes.
- [3] T. Kim, W. Song, D.-Y. Son, L.K. Ono, Y. Qi, Lithium-ion batteries: outlook on present, future, and hybridized technologies, 7 (2019) 2942–2964. doi:10.1039/c8ta10513h.
- [4] S.D. Beattie, M.J. Loveridge, M.J. Lain, S. Ferrari, B.J. Polzin, R. Bhagat, R. Dashwood, Understanding capacity fade in silicon based electrodes for lithium- ion batteries using three electrode cells and upper cut-off voltage studies, J. Power Sources. 302 (2016) 426–430. doi:10.1016/j.jpowsour.2015.10.066.
- [5] I. Ben-barak, Y. Kamir, S. Menkin, M. Goor, I. Shekhtman, T. Ripenbein, E. Galun, D. Golodnitsky, E. Peled, Drop-on-Demand 3D Printing of Lithium Iron Phosphate Cathodes, J. Electrochem. Soc. 166 (2019) 5059–5064. doi:10.1149/2.0091903jes.
- [6] P. Parikh, M. Sina, A. Banerjee, X. Wang, M.S.D. Souza, J. Doux, E.A. Wu, O.Y. Trieu, Y. Gong, Q. Zhou, K. Snyder, Y.S. Meng, Role of Polyacrylic Acid ( PAA ) Binder on the Solid Electrolyte Interphase in Silicon Anodes, (2019). doi:10.1021/acs.chemmater.8b05020.
- [7] D. Juarez-robles, C. Chen, Y. Barsukov, P.P. Mukherjee, Impedance Evolution Characteristics in Lithium-Ion Batteries, 164 (2017) 837–847. doi:10.1149/2.1251704jes.
- [8] K. Kierzek, J. Machnikowski, Factors influencing cycle-life of full Li-ion cell built from Si / C composite as anode and conventional cathodic material, Electrochim. Acta. 192 (2016) 475–481. doi:10.1016/j.electacta.2016.02.019.
- [9] S. Klink, E. Madej, E. Ventosa, A. Lindner, W. Schuhmann, F. La, The importance of cell geometry for electrochemical impedance spectroscopy in three-electrode lithium ion battery test cells, Electrochem. Commun. 22 (2012) 120–123. doi:10.1016/j.elecom.2012.06.010.
- [10] Z. Zhu, Y. Zhou, P. Yan, R.S. Vemuri, W. Xu, R. Zhao, X. Wang, In Situ Mass Spectrometric Determination of Molecular Structural Evolution at the Solid Electrolyte Interphase in Lithium-Ion Batteries, (2015). doi:10.1021/acs.nanolett.5b02479.

- [11] K. Ogata, E. Salager, C.J. Kerr, A.E. Fraser, C. Ducati, A.J. Morris, S. Hofmann, C.P. Grey, Revealing lithium–silicide phase transformations in nano-structured silicon-based lithium ion batteries via in situ NMR spectroscopy, *Nat. Commun.* 5 (2014) 1–11. doi:10.1038/ncomms4217.
- [12] D.P. Abraham, A.F. Bower, I. Yoon, P.R. Guduru, B.L. Lucht, In Situ Measurement of Solid Electrolyte Interphase Evolution on Silicon Anodes Using Atomic Force Microscopy, *Adv. Energy Mater.* 6 (2016) 1600099. doi:10.1002/aenm.201600099.
- [13] L. Leveau, B. Laïk, J.P. Pereira-Ramos, A. Gohier, P. Tran-Van, C.S. Cojocaru, Silicon nano-trees as high areal capacity anodes for lithium-ion batteries, *J. Power Sources.* 316 (2016) 1–7. doi:10.1016/j.jpowsour.2016.03.053.
- [14] M.S. Wang, W.L. Song, J. Wang, L.Z. Fan, Highly uniform silicon nanoparticle/porous carbon nanofiber hybrids towards free-standing high-performance anodes for lithium-ion batteries, *Carbon N. Y.* 82 (2015) 337–345. doi:10.1016/j.carbon.2014.10.078.
- [15] X. Yang, X. Gao, Q. Sun, S.P. Jand, Y. Yu, Y. Zhao, X. Li, K. Adair, L. Kuo, J. Rohrer, J. Liang, X. Lin, Promoting the Transformation of  $\text{Li}_2\text{S}_2$  to  $\text{Li}_2\text{S}$ : Significantly Increasing Utilization of Active Materials for High-Sulfur- Loading Li – S Batteries, 1901220 (2019) 1–10. doi:10.1002/adma.201901220.
- [16] Z. Yuan, H. Peng, J. Huang, X. Liu, D. Wang, X. Cheng, Hierarchical Free-Standing Carbon-Nanotube Paper Electrodes with Ultrahigh Sulfur-Loading for Lithium – Sulfur Batteries, (2014) 6105–6112. doi:10.1002/adfm.201401501.
- [17] D. Rehnlund, F. Lindgren, S. Böhme, T. Nordh, Y. Zou, J. Pettersson, U. Bexell, M. Boman, K. Edström, L. Nyholm, Lithium trapping in alloy forming electrodes and current collectors for lithium based batteries, *Energy Environ. Sci.* 10 (2017) 1350–1357. doi:10.1039/c7ee00244k.
- [18] F. Reuter, A. Baasner, J. Pampel, M. Piwko, H. Althues, S. Kaskel, S. Dörfler, Importance of Capacity Balancing on The Electrochemical Performance of  $\text{Li} [ \text{Ni}_{0.8} \text{Co}_{0.1} \text{Mn}_{0.1} ] \text{O}_2$  ( NCM811 )/ Silicon Full Cells, 166 (2019). doi:10.1149/2.0431914jes.
- [19] N. Harpak, G. Davidi, D. Schneier, S. Menkin, E. Mados, D. Golodnitsky, E. Peled, F. Patolsky, Large-Scale Self-Catalyzed Spongelike Silicon Nano-Network-Based 3D Anodes for High-Capacity Lithium-Ion Batteries, *Nano Lett.* (2019) acs.nanolett.8b05127. doi:10.1021/acs.nanolett.8b05127.
- [20] D. Schneier, N. Harpak, S. Menkin, G. Davidi, M. Goor, E. Mados, G. Ardel, F. Patolsky, D. Golodnitsky, E. Peled, Analysis of Scale-up Parameters in 3D Silicon-Nanowire Lithium-Battery Anodes Analysis of Scale-up Parameters in 3D Silicon-Nanowire Lithium- Battery Anodes, (2020). doi:10.1149/1945-7111/ab6f5a.
- [21] F. Nobili, F. Croce, B. Scrosati, R. Marassi, Electronic and Electrochemical Properties of  $\text{Li}_x \text{Ni}_{1-y} \text{Co}_y \text{O}_2$  Cathodes Studied by Impedance, (2001) 1642–1646. doi:10.1021/cm000600x.