Accepted Manuscript

Integration of High Capacity Materials into Interdigitated Mesostructured Electrodes for High Energy and High Power Density Primary Microbatteries

James H. Pikul, Jinyun Liu, Paul V. Braun, William P. King

PII: S0378-7753(16)30234-8

DOI: [10.1016/j.jpowsour.2016.03.034](https://doi.org/10.1016/j.jpowsour.2016.03.034)

Reference: POWER 22386

To appear in: *Journal of Power Sources*

Received Date: 5 January 2016

Revised Date: 9 February 2016

Accepted Date: 9 March 2016

Please cite this article as: J.H. Pikul, J. Liu, P.V. Braun, W.P. King, Integration of High Capacity Materials into Interdigitated Mesostructured Electrodes for High Energy and High Power Density Primary Microbatteries, *Journal of Power Sources* (2016), doi: 10.1016/j.jpowsour.2016.03.034.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Integration of High Capacity Materials into Interdigitated Mesostructured Electrodes for High Energy and High Power Density Primary Microbatteries

James H. Pikul^a, Jinyun Liu^b, Paul V. Braun^b, William P. King^{a,*}

^a Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801, USA
E-mail: jpikul2@illinois.edu, *wpk@illinois.edu
Phone: 217-244-3864, Fax: 217-244-9956

^b Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 West Green Street, Urbana, IL 61801, USA
E-mail: jyliu@illinois.edu, pbraun@illinois.edu

Abstract – Microbatteries are increasingly important for powering electronic systems, however, the volumetric energy density of microbatteries lags behind that of conventional format batteries. This paper reports a primary microbattery with energy density $45.5 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ and peak power $5,300 \mu\text{W cm}^{-2} \mu\text{m}^{-1}$, enabled by the integration of large volume fractions of high capacity anode and cathode chemistry into porous micro-architectures. The interdigitated battery electrodes consist of a lithium metal anode and a mesoporous manganese oxide cathode. The key enabler of the high energy and power density is the integration of the high capacity manganese oxide conversion chemistry into a mesostructured high power interdigitated bicontinuous cathode architecture and an electrodeposited dense lithium metal anode. The resultant energy density is greater than previously reported three-dimensional microbatteries and is comparable to commercial conventional format lithium-based batteries.

Keywords: microbattery, conversion electrode, lithium battery, lithium deposition, high power

1. Introduction

Integration of miniature sensors and radio devices into consumer goods, biomedical devices, and industrial electronics has driven significant interest in microbatteries [1]. Developments in electrode structure engineering have enabled secondary microbatteries with power densities 100 times greater than commercial lithium ion batteries (up to 7.4 mW cm^{-2}

μm^{-1}) [2-4]. The high power densities were achieved with interdigitated mesostructured electrode architectures that simultaneously reduced ion and electron transport resistances in the anode, cathode, and electrolyte. The electrodes consisted of thin films of electrochemically active materials coated on highly conductive porous metal current collectors, providing good electrical conductivity and reduced solid state ion diffusion distances [2, 3]. Electrode interdigitation reduced ion transport lengths across the electrolyte. As is true for all secondary batteries, the energy density was lower than a similarly sized primary battery. Given that for a number of microbattery applications recharging is not possible, the added energy density of a primary system is worth considering. Here we demonstrate how primary microbatteries with both high energy and power density can be realized by integrating large volume fractions of high capacity materials into high power microbattery architectures.

Integration of high capacity primary electrode materials into high power microbattery architectures is challenging. Electrochemically active material must be deposited with nanometer-scale thickness control throughout high surface area porous current collectors. Because of the interdigitated design, both the anode and cathode materials must be grown on the same substrate. Finally, prevention of electrical shorts between narrowly spaced electrodes is required. Gas-phase deposition methods (e.g. ALD and CVD) provide high quality conformal coatings but require complicated strategies to limit deposition to only the anode or cathode [4-6]. Electrodeposition techniques that take advantage of the electrical separation between anode and cathode have been used to deposit materials into high power secondary electrodes, but the lower capacity and volume fraction of the electrochemically active materials used limited the energy density [2, 3]. In a primary system, the materials constraints are reduced, since recharging is not necessary, enabling possible use of high capacity anode materials including silicon, tin ^[7], lithium [8-12], and conversion reaction based oxides [13-15]. For a primary battery, where dendrite growth and solid electrolyte interphase (SEI)

formation during cycling is not important, lithium is perhaps the most promising anode due to its high capacity, low density, and low reference voltage [8-12, 16-25]. On the cathode side, maximization of capacity and voltage is important, with the realization that most high capacity cathodes require high processing temperatures for crystallization that are not compatible with other microbattery components [13-15, 26]. A notable exception is manganese oxide, which has a high capacity, even in the electroplated version.

Here we integrate large volume fractions of high capacity materials (lithium anode and manganese oxide conversion cathode) into high power interdigitated 3D mesostructured bicontinuous microbattery architectures using near room temperature processing conditions, resulting in the formation of primary microbatteries with impressive energy and power. The primary microbatteries have $5,300 \mu\text{W cm}^{-2} \mu\text{m}^{-1}$ peak power density and up to $45.5 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ energy densities. The energy density is greater than previous 3D microbatteries and comparable to commercially available conventional format lithium based batteries [2, 27-29].

2. Experimental

2.1 Microbattery Fabrication

Figure 1c outlines the microbattery fabrication, which followed a similar procedure we developed for secondary microbatteries [2]. First, an interdigitated gold pattern that defined the geometry for the microbattery electrodes was fabricated by sputtering 8 nm of chromium followed by 70 nm of gold on a 1 mm thick soda lime glass slide, and then patterned and etched via conventional lithographic processing. The interdigitated gold pattern had 5 mm long and 5 μm wide parallel rectangles, called fingers, connected to two perpendicular 4 mm wide contact pads such that every other finger was electrically connected through a contact pad and neighboring fingers were electrically isolated. The glass slide with gold pattern was then cut into smaller samples, piranha cleaned for ten minutes, immersed in ultrapure water with 3-mercaptopropylsulfonic acid, sodium salt (2.2% by weight) for 3 hours and rinsed. Polystyrene (PS) opals were self-assembled onto the gold patterned substrate by first placing

the substrate vertically in 1 inch diameter plastic container filled with a colloid solution of 500 nm in diameter PS spheres. The plastic container was then set on a hotplate at 55° C, covered, and left for 24 to 30 hours until the solution was dry. The substrate was then sintered at 96 °C for 5 hours, which increased the contact area between the PS spheres to about 200 nm in diameter. This contact area determines the diameter of the holes, or interconnects, between the 500 nm pores in the inverted nickel current collector. A larger interconnect diameter allows for more active material deposition before the interconnect holes are pinched closed, which prevents the transport of ions through the porous structure. The PS colloidal solution was made by combining 8 wt% PS sphere solution (1.2 grams), purchased from Invitrogen, with ultrapure water (40 grams). The porous, bicontinuous nickel current collectors for the cathode electrodes were fabricated by electrodepositing nickel through the PS opal at a constant -1.8 V versus a nickel reference electrode in Technic RTU Mechanical Agitation commercial plating solution. In this step, the anode and cathode current collectors were independently deposited for 2 minutes and 12 minutes. The deposition time controlled the anode and cathode current collector sizes. The nickel anode current collector provided a barrier between the gold and lithium that was later deposited, as lithium electrochemically alloys with gold at the lithium deposition voltage. PS was removed by immersing the substrates in a tetrahydrofuran bath for 24 hours followed by a tetrahydrofuran and toluene rinse. The resulting nickel current collectors provided the architecture for the microbattery. The cathode current collectors are typically 33 μm wide, 15 μm tall, and 87% porous, separated between 5 μm wide and less than 1 μm tall interdigitated anode current collectors.

2.2 Electrochemically active material electrodeposition

The cathode and anode electrochemically active materials were independently electrodeposited onto the electrically isolated nickel current collectors. The cathode current collector was first primed for manganese deposition by applying 15 cycles of 1.2 and -0.5 V pulsed vs. Ag/AgCl for 0.1 and 3.0 seconds in ultrapure water with manganese acetate

tetrahydrate (0.1 M) and sodium sulfate (0.1 M) titrated to pH 5.5 using sulfuric acid. Manganese oxide was then deposited and partially stripped for 30 cycles by applying 0.6 V vs. Ag/AgCl for 8 seconds followed by -0.95 and -0.8 V for 2 seconds each, with a 25 second open circuit rest between each cycle. After deposition, the manganese oxide was electrochemically oxidized by holding the cathode at 1.1 V vs. Ag/AgCl for ten minutes in ultrapure water titrated to pH 3.5 using sulfuric acid.

A 1 mm thick polyethylene gasket with acrylic adhesive and a 0.5 mm² through hole was placed on the microbattery substrate to enable precise measurement of the microbattery area after discharge. Only the electrodes beneath the through hole are exposed to the electrolyte. The substrate was preheated to 110 °C before the mask was added to improve the mask adhesion and prevent electrolyte from leaking to other areas of the electrodes. The microbattery substrate was moved to an argon filled glovebox. Lithium was then deposited onto the anode current collector at 0.75 mA cm⁻² current density with LiClO₄ (1.0 M) and CsPF₆ (0.05 M) in 80% propylene carbonate (PC) solution with 20% vinylene carbonate (VC) based on a recipe from Ding et al. [8]. VC was added to form a thin SEI film and suppress the deleterious reaction between the deposited lithium and the electrolyte [11]. The solution was made by first mixing AgPF₆ (0.05 M) with CsI (0.05 M) in PC (25 ml), and stirring for 12 hours in an argon filled glovebox. After mixing, AgI formed a yellow precipitate that was filtered out by running the solution through a 0.45 µm syringe filter. A piece of lithium was then inserted into the solution to react any excess silver ions followed by another filtration step. VC (5 ml) was then added along with LiClO₄ (1 M), after which the solution was filtered and ready for lithium deposition. The cycling efficiencies reported in Table 1 were determined by galvanostatically depositing lithium on a flat nickel substrate for set period of time, typically 1 hour, and then galvanostatically de-plating lithium at the same current density until the sample potential reached 0.2 V versus lithium. The cycling efficiency was determined by

dividing the coulombs de-plated by the total deposited coulombs. The reported numbers in Table 1 represent the best performance for each electrolyte.

2.3 Electrochemical characterization

The completed microbatteries were galvanostatically discharged to 0.5 V vs. a lithium reference at various current densities and pulsed sequences in 1:1 EC:DMC liquid electrolyte with 1 M LiClO₄. The energy and power density of the microbattery cells were calculated by measuring the discharge voltage and current and normalizing the total energy and power to the volume of the microbattery cell, which includes the total volume occupied by the electrodes (anode, cathode, Ni current collector, and electrolyte in the porous 3D electrode) and the electrolyte in the separation between the electrodes. The volume was calculated by multiplying the height of the electrodes by the cell area, which was measured in a SEM.

3. Results and Discussion

3.1 Integration

Figure 1a shows the interdigitated electrode architecture. The cathode is a composite electrode composed of a highly porous bicontinuous nickel current collector conformally coated with high volume fractions of manganese oxide. The anode is densely electroplated lithium metal. Figure 1b shows scanning electron microscope images of the microbattery electrodes. The electrodes are 15 μm tall, 33 μm wide, and 45 μm center-to-center. This architecture is chosen to enable high power density by reducing ion and electron transport resistances [2, 3, 30, 31]. The bicontinuous cathode offers short solid-state lithium diffusion lengths through the manganese oxide and highly conductive continuous electron pathways in the nickel current collector. The bicontinuous current collector is not necessary in the lithium metal anode because lithium is electrically conductive and undergoes a de-plating reaction with no solid-state diffusion. The interdigitated electrodes minimize polarization in the electrolyte by shortening ion diffusion and migration distances between electrodes [3].

Manganese oxide is used as the cathode because of its high irreversible conversion

chemistry-based capacity, ~1 V average potential versus lithium, and because it can be grown electrochemically near room temperature [13-15]. Lithium is used as the anode due to its high capacity and low, constant reference voltage which is important when using lower voltage cathodes. We suggest, should higher voltages be needed for application, that the battery voltage can be up converted to a constant 1.8 to 5.5 V at greater than 90% efficiency using recently developed boost converters, e.g. a Texas Instruments tps61200 [32].

3.1.1 Manganese oxide cathode

The manganese oxide was integrated into the microbattery architecture using electrodeposition. A key requirement for high energy density was to fill most of the free volume within the metal scaffold current collector without compromising the electrode features that enable high power. The bicontinuous current collector initially had 500 nm diameter pores which were reduced as manganese oxide was deposited onto the nickel, until they finally are pinched closed. If the manganese oxide deposition was not conformal, the closed pores in one region of the electrode would prevent lithium ions from flowing to the rest of the electrode volume. To achieve conformal coating of manganese oxide in the porous nickel scaffold, the manganese oxide was cycled between additive electrochemical deposition and subtractive electrochemical stripping. Figure 2a shows the voltage profile and resulting current for two cycles of the voltage controlled electrodeposition and electrochemical stripping process. Manganese oxide was deposited at 0.6 V vs. Ag/AgCl for eight seconds followed by stripping at -0.95 and -0.8 V for 2 seconds each and open circuit for 25 seconds (0 mA). The voltage regulated the rate of material deposition or stripping and the time controlled the total deposit thickness. Similar to the time delay in transmission lines, the deposition of manganese oxide in porous media had a time delay where the electrolyte capacitance caused the oxide to preferentially deposit or strip at the electrode top near the bulk electrolyte [33]. The two stripping voltages in Fig. 2a took advantage of the time delay. The -0.95 V etch for 2 seconds stripped a large amount of oxide mostly near the electrode top.

Reducing the etch voltage to -0.8 V for the last 2 seconds reduced the amount of stripping at the electrode middle and bottom. This combination resulted in conformal deposition, and enabled nearly complete infilling while leaving sufficient pores for ion motion through the electrode. This is in contrast to if the voltage was held at -0.95 V for the entire 4 seconds, which caused over etching in the middle and bottom electrode, resulting in a gradient in oxide thickness from top to bottom. Figure 2b shows top, middle, and bottom SEMs of an electrode after 30 cycles of deposition and stripping using the optimized the waveform in Fig. 2a. The thickness of the oxide in the bottom and middle of the electrode was 40 – 50 nm, corresponding to 29% – 36% volume fraction of manganese oxide. The oxide coating was thinnest at the top, which was beneficial for high power density as the thin oxide allows larger volumes of electrolyte in the structure, and reduced the time for ions to diffuse to the interior of the electrode.

If stripping was not used, or the electrode was excessively stripped, very non-uniform manganese oxide deposition was observed. Figure 2c shows an electrode cross-section when stripping was not used during manganese oxide deposition. The manganese oxide layer was 500 nm thick at the electrode top and only a few nanometers thick at the electrode bottom. In this experiment, manganese oxide was deposited using 10 cycles of 0.6 V for 4 seconds followed by open circuit for 25 seconds. Reducing the applied voltage time to less than a second did not significantly improve the uneven oxide deposition, indicating that the gradient in oxide thickness was not due to ion diffusion limitations in the electrolyte. The voltage, time, and duration between pulses controlled the location of the thickest layer of manganese oxide as illustrated by the following experiment. Figure 2d shows the cross section of an electrode deposited using 29 cycles of 0.6 V for 8 seconds followed by -0.8 V for 2 seconds, open circuit for 10 seconds, -0.95 V for 3 seconds, and open circuit for 25 seconds. The manganese oxide thickness alternated from thin on the electrode bottom to thick in the middle and thin again at the electrode top. The open circuit duration between stripping voltages

caused most of the stripping to occur at the electrode top, compared to the result in Fig. 2a with no off time, which resulted in conformal deposition. Under proper conditions, the pulsed deposition and stripping of manganese oxide enabled highly conformal and thick deposition, enabling a high active material volume fraction. Most electrodes investigated were 30 - 40% manganese oxide by volume, with a maximum of 50% manganese oxide by volume achieved. The mass loading of manganese oxide was $1.5 - 2.0 \text{ g cm}^{-3}$.

3.1.2 Lithium anode

The lithium anode was grown from an electrolyte of LiClO_4 and CsPF_6 in propylene carbonate/vinylene carbonate. Initially, depositing thick and dense lithium metal films without forming electrical shorts between the deposited lithium and cathode was challenging because of dendritic growth, leading to selection of this deposition chemistry [8-12]. Table 1 gives the electrolytes tested for lithium plating and the plating coulombic efficiencies as measured by the capacity extracted from the deposited lithium compared to the charge during the plating process. Some electrolytes had coulombic efficiencies as high as 80%, probably due to the formation of a thin, solid SEI, which prevented the deposited lithium from further reacting with the electrolyte; however, these electrolytes still formed dendrites which shorted the battery before a large amount of lithium could be deposited. To suppress dendrite formation cesium salts were added to the electrolyte. Cesium ions have been reported to ionically shield the dendritic tips, smoothing the deposited lithium [8]. Figure 3a shows the voltage during lithium deposition from an electrolyte consisting of 1 M LiClO_4 and 0.05 M CsPF_6 in 80% v/v propylene carbonate and 20% v/v vinylene carbonate at 0.75 mA cm^{-2} of interdigitated anode area. The voltage is kept above negative 0.1 V, which is the reduction voltage of 0.05 M Cs^+ relative to 1 M Li^+ versus lithium [8]. Figure 3b shows lithium dendrites formed after lithium deposition in this electrolyte. Figure 3c shows dendrites formed when lithium was deposited using 1 M LiClO_4 in cesium-free 1:1 EC:DMC electrolyte (a common battery electrolyte), which is indicative of the dendrite formation in cesium-free electrolytes. The

dendrites formed in cesium-containing electrolytes were generally shorter, thicker, and less porous than those deposited without cesium. The increased density of the dendrites formed in the cesium based electrolyte led to significantly higher anode capacities than lithium anodes deposited using electrolytes with high columbic efficiency but thinner and more porous dendrites.

3.2. Electrochemical Performance

Figure 4a shows a galvanostatic discharge curve for a primary microbattery between 3.2 and 0.5 V. The voltage decreased more rapidly down to 1.4 V, and then more slowly after that. The manganese oxide discharge curves compare well to the first discharge of previously reported Mn_2O_3 and Mn_3O_4 electrodes [13-15, 34]. The large slope in the discharge curve from 3.2 to 1.4 V was from an intercalation reaction in the cathode [13-15, 34]. The cathode then underwent conversion of the manganese oxide to lithium oxide and SEI formation reactions from 1.4 to 0.5 V that account for 85% of the total capacity. The capacity due to SEI formation and other irreversible reactions was approximated by comparing the first and second discharge cycles of manganese oxide processed on a thin film of nickel. The manganese oxide was cycled between 3.5 and 0.25 V to reduce the manganese oxide without reducing the gold under the nickel current collectors. The capacity of the first and second discharge at 0.5 V were compared, and not the capacity at 0.25 V, because of the 0.5 V shutoff used in the full microbattery cell. The capacity at 0.5 V was 2.25 times greater in the first cycle than the second cycle, indicating SEI formation and other irreversible reactions in the cathode enhanced the capacity of the full microbattery by about 100% when discharged to 0.5 V. The 100% capacity enhancement in the first cycle is larger in the bicontinuous electrode architecture than the 50% capacity enhancement in slurry cast Mn_2O_3 and Mn_3O_4 [13, 14]. The capacity of the first discharge at 0.5 V was 1.4 times greater than the reversible capacity at 0.25 V, indicating the capacity of the first manganese oxide discharge to 0.5 V was similar to the 800 mAh g^{-1} reversible capacity reported for conversion reaction based

manganese oxides [13-15, 34].

The microbatteries maintain a high energy density when discharged at high average power densities up to $2,300 \mu\text{W cm}^{-2}\mu\text{m}^{-1}$. Figure 4b shows the voltage of a full cell discharged at various current densities. The voltage initially fell quickly as the battery was discharged at high rate until it reached 0.5 V. The battery was then discharged at lower rates until the full capacity was extracted, with 5 – 10 minutes of open circuit between discharges. The black curve shows the lithium anode voltage versus a lithium reference electrode during the discharge. Near the end of discharge the lithium voltage increased dramatically. The total energy extracted for each discharge rate was the sum of the energy extracted at that rate and the energy extracted for all previous higher power rates. This approach enabled accurate rate performance data for batteries that can only be discharged once [35]. The average power densities at each discharge were 2,300, 790, 120, 40, 15, 4, and $1 \mu\text{W cm}^{-2}\mu\text{m}^{-1}$, with corresponding energy densities of 0.3, 1.9, 5.0, 7.8, 11.3, 19.7, and $45.5 \mu\text{Wh cm}^{-2}\mu\text{m}^{-1}$. Discharging the microbatteries to a cut-off voltage lower than 0.5 V could further improve the energy density; however, the sharp increase in anode voltage at the end of discharge shows the energy density is limited by the amount of lithium deposited.

In addition to high constant current discharges, the microbatteries were discharged with multiple high pulsed currents, which may more closely mimic microbattery use in sensor and wireless communication applications. Figure 4c shows a segment of a microbattery discharge curve during pulsed discharge. The same voltage profile as Fig. 4a can be seen with the addition of sharp decreases in voltage corresponding to high current discharges. The microbatteries had a 0.0 V shut-off limit to mimic scenarios where high power and high depth of discharge are needed. The first pulsed discharge was a 50 millisecond $1950 \mu\text{A cm}^{-2}\mu\text{m}^{-1}$ current for 120 cycles, with a constant current discharge of $0.3 \mu\text{A cm}^{-2}\mu\text{m}^{-1}$ between pulses. The battery was then discharged for 50 milliseconds at $970 \mu\text{A cm}^{-2}\mu\text{m}^{-1}$ for 180 cycles, with an open circuit between pulses. Figure 4d shows two cycles for each of these pulses. The

microbattery voltage returned to approximately 75% of its pre-high rate discharge voltage within 1 second of rest under both pulsed discharge conditions. The discharge performance shows that the microbatteries can alternate between supercapacitor equivalent high power pulsed discharges and low power / high energy sleep discharges, which is important for many wireless and remote system applications.

Figure 5 shows the average power density versus energy density of two full microbattery cells tested at multiple discharge rates. The data is presented on a Ragone plot to compare it to other energy storage technologies, including high power rechargeable microbatteries previously published by us [2]. At low power, the two primary microbatteries have 44.7 and 45.5 $\mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ energy densities. At high power the primary microbatteries have similar energy and power density performance to our previous secondary microbatteries, which is ~100 X higher power density than other 3D microbatteries. The low rate energy densities corresponds to 2X the energy density of the best 3D secondary microbatteries, with the exception of work done by Lai et al. which achieved a cyclable 40 $\mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ energy density [27-29]. The primary microbatteries have similar energy densities to commercially available lithium/manganese oxide based primary batteries with a ~50 X higher peak power density.

4. Conclusions

Primary microbatteries made from high capacity, low voltage materials integrated into high power architectures achieved 45.5 $\mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ energy and 5,300 $\mu\text{W cm}^{-2} \mu\text{m}^{-1}$ peak power density. The interdigitated 3D mesostructured bicontinuous architecture enabled ultra-high power density. Proper electrochemical deposition strategies for the 3D mesoporous current collector and dense lithium anode deposition, coupled with judicious electrochemically active material choices enabled a high energy density. This demonstration of applying high energy density primary chemistry to the high power micro architecture provides confidence that the micro architecture concept can be extended to other battery

chemistries to achieve ultra-high power density while maintaining commercial battery equivalent energy densities. The combination of high energy and power density primary microbatteries may be attractive for many devices, including medical, military, and industrial devices that require smaller power sources, faster computation, stronger actuation, long-range telemetry or high current therapy modalities [17, 18].

Acknowledgements

This research is supported in part by the Department of Energy Office of Science Graduate Fellowship Program (DOE SCGF), made possible in part by the American Recovery and Reinvestment Act of 2009, administered by ORISE-ORAU under contract no. DE-AC05-06OR23100, and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award # DE-FG02-07ER46471.

References

- [1] V. Narain, Global thin-film batteries (TFB) market, Frost and Sullivan, (2013) 1-53.
- [2] J.H. Pikul, H. Gang Zhang, J. Cho, P.V. Braun, W.P. King, Nat. Commun., 4 (2013) 1732.
- [3] H. Ning, J.H. Pikul, R. Zhang, X. Li, S. Xu, J. Wang, J.A. Rogers, W.P. King, P.V. Braun, Proceedings of the National Academy of Sciences, (2015).
- [4] C. Liu, E.I. Gillette, X. Chen, A.J. Pearce, A.C. Kozen, M.A. Schroeder, K.E. Gregorczyk, S.B. Lee, G.W. Rubloff, Nat Nano, 9 (2014) 1031-1039.
- [5] T.S. Arthur, D.J. Bates, N. Cirigliano, D.C. Johnson, P. Malati, J.M. Mosby, E. Perre, M.T. Rawls, A.L. Prieto, B. Dunn, MRS Bulletin, 36 (2011) 523-531.
- [6] J.W. Long, B. Dunn, D.R. Rolison, H.S. White, Chemical Reviews, 104 (2004) 4463-4492.
- [7] B.A. Boukamp, G.C. Lesh, R.A. Huggins, J. Electrochem. Soc., 128 (1981) 725-729.
- [8] F. Ding, W. Xu, G.L. Graff, J. Zhang, M.L. Sushko, X. Chen, Y. Shao, M.H. Engelhard, Z. Nie, J. Xiao, X. Liu, P.V. Sushko, J. Liu, J.-G. Zhang, J. Am. Chem. Soc., 135 (2013) 4450-4456.
- [9] S.-i. Tobishima, T. Okada, Electrochim. Acta, 30 (1985) 1715-1722.
- [10] G. Zheng, S.W. Lee, Z. Liang, H.-W. Lee, K. Yan, H. Yao, H. Wang, W. Li, S. Chu, Y. Cui, Nat Nano, 9 (2014) 618-623.
- [11] H. Ota, K. Shima, M. Ue, J.-i. Yamaki, Electrochim. Acta, 49 (2004) 565-572.
- [12] Z. Tu, Y. Kambe, Y. Lu, L.A. Archer, Adv. Energy Mater., 4 (2014) n/a-n/a.
- [13] Y. Deng, Z. Li, Z. Shi, H. Xu, F. Peng, G. Chen, RSC Advances, 2 (2012) 4645-4647.
- [14] J. Gao, M.A. Lowe, H.D. Abruña, Chem. Mater., 23 (2011) 3223-3227.
- [15] L. Chang, L. Mai, X. Xu, Q. An, Y. Zhao, D. Wang, X. Feng, RSC Advances, 3 (2013) 1947-1952.
- [16] World primary lithium battery market, Frost and Sullivan, (2009).
- [17] G. Blomgren, Encyclopedia of Applied Electrochemistry, (2014) 1720-1723.
- [18] P.A. Tamirisa, K. Chen, G. Jain, Encyclopedia of Applied Electrochemistry, (2014) 1713-1720.
- [19] C.C. Liang, J. Epstein, G.H. Boyle, J. Electrochem. Soc., 116 (1969) 1452-1454.
- [20] A. Piqué, C.B. Arnold, H. Kim, M. Ollinger, T.E. Sutto, Appl Phys A, 79 (2004) 783-786.

- [21] C.B. Arnold, H. Kim, A. Piqué, Appl Phys A, 79 (2004) 417-420.
- [22] F. Albano, Y.S. Lin, D. Blaauw, D.M. Sylvester, K.D. Wise, A.M. Sastry, J. Power Sources, 185 (2008) 1524-1532.
- [23] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans, Solid State Ionics, 135 (2000) 33-45.
- [24] P.H. Humble, J.N. Harb, R. LaFollette, J. Electrochem. Soc., 148 (2001) A1357-A1361.
- [25] K.T. Braam, S.K. Volkman, V. Subramanian, J. Power Sources, 199 (2012) 367-372.
- [26] J.B. Goodenough, Y. Kim, Chem. Mater., 22 (2009) 587-603.
- [27] K. Yoshima, H. Munakata, K. Kanamura, J. Power Sources, 208 (2012) 404-408.
- [28] K. Sun, T.-S. Wei, B.Y. Ahn, J.Y. Seo, S.J. Dillon, J.A. Lewis, Advanced Materials, 25 (2013) 4539-4543.
- [29] W. Lai, C.K. Erdonmez, T.F. Marinis, C.K. Bjune, N.J. Dudney, F. Xu, R. Wartena, Y.-M. Chiang, Advanced Materials, 22 (2010) E139-E144.
- [30] H. Zhang, X. Yu, P.V. Braun, Nat. Nanotechnol., 6 (2011) 277-281.
- [31] P.V. Braun, J. Cho, J.H. Pikul, W.P. King, H. Zhang, Curr. Opin. Solid State Mater. Sci., 16 (2012) 186-198.
- [32] TPS61200, November 29, (2015), Web. <http://www.ti.com/product/tps61200>
- [33] S. Wu, X. Liu, T. Hu, J. Jiang, P.K. Chu, K.W.K. Yeung, C.Y. Chung, C.L. Chu, Z. Xu, W.W. Lu, K.M.C. Cheung, K.D.K. Luk, J. Electrochem. Soc., 156 (2009) C187-C194.
- [34] H. Wang, L.-F. Cui, Y. Yang, H. Sanchez Casalongue, J.T. Robinson, Y. Liang, Y. Cui, H. Dai, J. Am. Chem. Soc., 132 (2010) 13978-13980.
- [35] M. Doyle, J. Newman, J. Reimers, J. Power Sources, 52 (1994) 211-216.

Figure 1. (a) The microbattery design, consisting of high capacity anode and cathode chemistry integrated into an interdigitated 3D mesostructured bicontinuous architecture that enables high power and high energy density. The mesoporous cathode is conversion reaction based manganese oxide (red) coated on an electrically conductive bicontinuous nickel current collector (blue). The anode is electrodeposited lithium. (b) Scanning electron microscope images of the interdigitated electrodes. The inset shows an anode and cathode cross-section. (c) Microbattery fabrication process. Polystyrene spheres are first self-assembled on to a gold coated glass substrate followed by nickel electrodeposition through the polystyrene. The polystyrene is then etched and manganese oxide is conformally coated on the porous nickel current collector. Lithium is then densely electrodeposited on the other nickel current collector using a cesium salt based electrolyte.

Figure 2. (a) The applied voltage and resulting current vs. time of the pulsed manganese oxide deposition technique. Manganese oxide deposits under positive applied voltage and is stripped under negative applied voltage to ensure a conformal coating on the mesoporous nickel scaffold. (b) SEM cross sections of the top, middle, and bottom of a microbattery cathode after deposition with the voltage profile in (a). (c) An SEM of an electrode cross section when no stripping is used. (d) An SEM of an electrode cross section where the thickest manganese oxide is deposited in the center of the electrode illustrating the ability to specifically engineer the thickness of the manganese oxide across the electrode depth. (e) TEM and selected area diffraction images of the manganese oxide showing polycrystalline nanometer-sized grains.

Figure 3. (a) Voltage versus time for lithium deposition at 0.75 mA cm^{-2} using 1 M LiClO_4 and 0.05 M CsPF_6 in 80% propylene carbonate and 20% vinylene carbonate. The voltage is versus lithium. Top view SEMs of (b) lithium deposited in (a), and (c) lithium deposited using 1M LiClO_4 in 1:1 ethylene carbonate : dimethyl carbonate, a conventional Li-ion battery electrolyte.

Figure 4. (a) A microbattery discharge curve. (b) A microbattery sequentially discharged at high to low current density with 5 – 10 minutes open circuit rests in between discharges. The peak energy and power densities are $45.5 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ and $5,300 \mu\text{W cm}^{-2} \mu\text{m}^{-1}$. (c) The first 21 hours of a microbattery discharged with short, very high current pulses indicative of use in possible sensing and wireless communication applications. (d) Expanded sections of the pulsed discharge curve for the microbattery in (c). The black curve shows the battery voltage after 50% depth of discharge during a 50 ms high current pulse ($1950 \mu\text{A cm}^{-2} \mu\text{m}^{-1}$), followed by a 2 minute open circuit rest and 15 minute low power discharge. The red curve shows the battery voltage after 85% depth of discharge during a $970 \mu\text{A cm}^{-2} \mu\text{m}^{-1}$ pulse for 50 ms, followed by a 2 minute open circuit rest.

Figure 5. A Ragone plot comparing the power and energy density of the two primary microbatteries (red and blue) to other technologies. The cathode half-cell is shown in black, along with recently published secondary microbatteries plotted at their highest energy density (MB1 through MB3). The plot also includes in the background the performance range of commercially available energy storage technologies and lithium/manganese oxide primary batteries from SAFT and DURACELL. The SAFT cell is plotted at the maximum energy density, $42 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$, and maximum recommended power, $34 \mu\text{W cm}^{-2} \mu\text{m}^{-1}$. While the SAFT max energy and power are plotted together, the achievable energy at the maximum power is not reported, but is probably less than $42 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$. The primary microbatteries have comparable energy density to commercially available primary batteries and 50X higher power densities, comparable to supercapacitor power densities.

Table 1. Cycling efficiency of electrolytes tested for lithium metal deposition

Solvent	Salt	Cycling Efficiency [%]
2-methyltetrahydrofuran	1.5 M LiAsF ₆	80
2-methyltetrahydrofuran w/ 1 % 2-methylfuran	1.5 M LiAsF ₆	59
1:1 ethylene carbonate : 2-methyltetrahydrofuran	1.5 M LiAsF ₆	66
2-methyltetrahydrofuran	1 M LiPF ₆	< 10
1:1 ethylene carbonate : tetrahydrofuran	1 M LiPF ₆	66
1,3-dioxolane	1.5 M LiAsF ₆	69
dimethyl sulfoxide	1 M LiPF ₆	47
propylene carbonate	1 M LiClO ₄	60
propylene carbonate w/ 0.05 M CsPF ₆	1 M LiPF ₆	43
propylene carbonate w/ 0.05 M CsPF ₆	1 M LiClO ₄	48
propylene carbonate w/ 20% vinylene carbonate & 0.05 M CsPF ₆	1 M LiClO ₄	45

Highlights for:**Integration of High Capacity Materials into Interdigitated Mesostructured Electrodes for High Energy and High Power Density Primary Microbatteries**

James H. Pikul^a, Jinyun Liu^b, Paul V. Braun^b, William P. King^{a,}*

^aDepartment of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801, USA

E-mail: jpikul2@illinois.edu, *wpk@illinois.edu

Phone: 217-244-3864, Fax: 217-244-9956

^bDepartment of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 West Green Street, Urbana, IL 61801, USA

E-mail: jyliu@illinois.edu, pbraun@illinois.edu

- Ultra-high power density is achieved in primary microbatteries.
- Integration of high capacity materials enables high energy density.
- Conformal electrodeposition in mesostructured electrodes is demonstrated.
- Dense lithium metal electrodeposition is demonstrated.