CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2009,** *21,* 3017–3020 3017
DOI:10.1021/cm900905e

Room Temperature Synthesis of the Larger Power, High Silver Density Cathode Material $Ag_4V_2O_6F_2$ for Implantable Cardioverter Defibrillators

Thomas A. Albrecht,[†] Frédéric Sauvage,[†] Vincent Bodenez,[‡] Jean-Marie Tarascon,[‡] and Kenneth R. Poeppelmeier*,[†]

[†] *Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, and* [‡] *LRCS, UMR CNRS 6007, Université de Picardie Jules Verne, 33 rue St. Leu, 80039 Amiens CEDEX, France*

Received April 1, 2009. Revised Manuscript Received May 6, 2009

New cathode materials will lead to technological advances for implantable cardioverter defibrillators, ICDs, such as reduced size and increased performance of the device. While the industry standard silver vanadium oxide $Ag_2V_4O_{11}$ exhibits great chemical/electrochemical stability, dense silver oxide fluoride materials are advantageous because of high crystal density that can result in an increased capacity above 3 V. This report highlights the reactivity at room temperature between Ag_2O and V_2O_5 in an aqueous HF solution which affords a rapid precipitation of sub-micrometer sized $Ag_4V_2O_6F_2$ (SVOF), a high capacity Li-battery cathode material. This system opens new and novel synthetic strategies in the design of new oxide fluoride materials.

Introduction

Implantable biomedical devices address a variety of needs including nerve/neuron stimulation, drug delivery, or cardiac management. The energy source, provided by an implanted battery which converts chemical energy to electrical energy, requires specific characteristics in accordance with the application targeted. Depending on power requirements, a variety of lithium-based primary batteries can be implemented, such as $Li-I_2$, $Li-SOCl_2$, or $Li-Ag_2V_4O_{11}$ (ε-SVO) for pacemakers, neuro-stimulators, or implantable cardioverter defibrillators (ICDs), respectively.[1] An ICD is a device implanted in a patient's chest who is at risk of tachycardia. The device, which continuously monitors the cardiac beat, can serve similarly to a pacemaker by delivering low-energy stimuli (50−100 μW) or addresses ventricular fibrillation by administering a vigorous electrical shock of as high as 30−40 J at 700 − 800 V to the right ventricle.[2,3] The ε-SVO cathode became the choice material for the ICD battery market since the original proposal from Keister et al. in 1984.[4] Ever since, the importance of ε-SVO as the foremost cathode has grown because it fulfills the stringent requirements of high chemical/electrochemical stability and high electrochemical behavior predictability together with exhibiting high discharge rate capability owing to its great electronic/ionic conduction ($\sigma_{e-} \sim 10^{-2}-10^{-3}$ S/cm and $D_{(Li+)} \sim 10^{-8}$ cm^2/s).[5−8]

Many advances have brought the Li-SVO system to its present maturity, including improved separator thinness, synthetic procedures, and particle/electrolyte interface.[9−14] Further progress in this area would stem from the design of a new cathode material which would (i) uptake lithium at higher potential and (ii) display a greater phase density to decrease capacitor charge time and battery size, respectively, while maintaining the high chemical/electrochemical cathode stability. With this in mind, our effort was concentrated on the exploration of dense silver oxide fluoride materials, in particular in the vanadium system. $Ag_4V_2O_6F_2$ (SVOF), the first silver vanadium oxide fluoride material, was synthesized in the $Ag_2O/V_2O_5/HF_{(aq)}$ system and exhibits electronic conductivity ($\sigma_{e-} = 5\times10^{-4}$ S/cm)

---

*Corresponding author. E-mail: krp@northwestern.edu.

(1) Brodd, R. J.; Bullock, K. R.; Leising, R. A.; Middaugh, R. L.; Miller, J. R.; Takeuchi, E. *J. Electrochem. Soc.* **2004**, *151*, K1–K11.
(2) Skarstad, P. M. *J. Power Sources* **2004**, *136*, 263–267.
(3) Crespi, A. M.; Somdahl, S. K.; Schmidt, C. L.; Skarstad, P. M. *J. Power Sources* **2001**, *96*, 33–38.
(4) Keister, P.; Mead, R. T.; Ebel, S. J.; Fairchild, W. R. *Proc. Power Sources Symp.* **1984**, *31st*, 331–338.
(5) Onoda, M.; Kanbe, K. *J. Phys.: Condens. Matter* **2001**, *13*, 6675–6685.
(6) Leising, R. A.; Thiebolt, W. C.; Takeuchi, E. S. *Inorg. Chem.* **1994**, *33*, 5733–40.
(7) Ramasamy, R. P.; Feger, C.; Strange, T.; Popov, B. N. *J. Appl. Electrochem.* **2006**, *36*, 487–497.
(8) Lee, J.-W.; Popov, B. N. *J. Power Sources* **2006**, *161*, 565–572.
(9) Leising, R. A.; Takeuchi, E. S. *Chem. Mater.* **1994**, *6*, 489–495.
(10) Zhang, S.; Li, W.; Li, C.; Chen, J. *J. Phys. Chem. B* **2006**, *110*, 24855–24863.
(11) Beninati, S.; Fantuzzi, M.; Mastragostino, M.; Soavi, F. *J. Power Sources* **2006**, *157*, 483–487.
(12) Takeuchi, K. J.; Marschilok, A. C.; Leising, R. A.; Takeuchi, E. S. *Mater. Res. Soc. Symp. Proc.* **2007**, *972*, 351–356.
(13) Leising, R.; Takeuchi, E. S. U.S. Patent 7,211,349, May 1, **2007**.
(14) Takeuchi, K. J.; Marschilok, A. C.; Davis, S. M.; Leising, R. A.; Takeuchi, E. S. *Coord. Chem. Rev.* **2001**, *219*, 283–310.

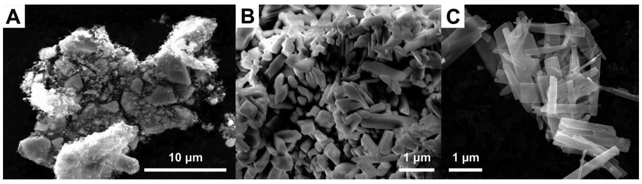

Figure 1. Scanning electron microscopy micrographs of particles used as cathode in lithium batteries (a) $Ag_4V_2O_6F_2$ synthesized by hydrothermal method (SVOF-Hyd), (b) $Ag_4V_2O_6F_2$ precipitated at room temperature (SVOF-RT), and (c) $Ag_2V_4O_{11}$ synthesized under hydrothermal conditions (ε-SVO).

and electrochemical activity vs lithium.[15] In particular, silver reduction occurs near 3.45 V (vs Li^+/Li), and the higher crystal structure density gives rise to a larger power density and volumetric capacity for SVOF and SVO ($\rho = 6.03$ g/cm^3 vs 4.80 g/cm^3 for SVO, respectively) and the recently reported phosphate ($Ag_2VO_2PO_4$, $\rho = 5.32$ g/cm^3).[16,17] Nevertheless, the large particle size resulting from the reported hydrothermal synthesis of SVOF (> 1 mm single crystals and > 10 μm after manually grinding, Figure 1a) hinders high discharge rate capability owing to ionic conduction limitations during the Ag^+/Li^+ displacement reaction.[18] One approach for improvement, which is the focus of this paper, is to drastically reduce the particle size to minimize the ion motion length in the solid.

Soft chemistry approaches have gained research interests for two reasons. First, these methods allow material to be accurately tailored (with regards to particle size, texture, morphology, porosity, etc.) through different thermodynamic parameters such as pH, temperature, or precursor concentration. The second driving force stems from an environmental aspect where a low temperature approach is synonymous with energy savings for large-scale chemical transformations. Among the different solvents and/or mineralizers used in solution chemistry, aqueous HF has received little attention while fluorides,[19,20] oxyfluorides,[21,22] or fluorophosphates[23,24] show promise as new cathode materials for Li-ion batteries. Moreover, what is presented here is the first room temperature synthesis of a cathode material, $Ag_4V_2O_6F_2$ (SVOF-RT), and for lithium batteries, in addition to a new silver vanadium oxide fluoride $Ag_3VO_2F_4$.[25,26]

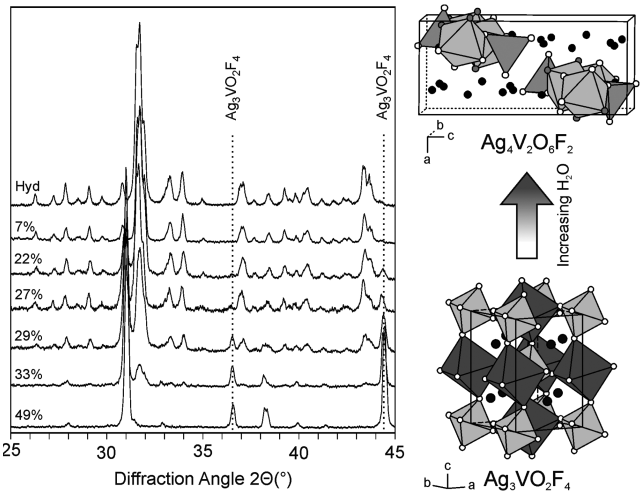

Figure 2. Series of powder X-ray diffractograms from reactions with a decreasing $HF_{(aq)}$ concentration (from the bottom up). $Ag_3VO_2F_4$ is formed with concentrated $HF_{(aq)}$ and phase pure $Ag_4V_2O_6F_2$ at 7% HF concentration. Diffractogram from a hydrothermal reaction, which yielded $Ag_4V_2O_6F_2$, is shown at the top for comparison. Two dotted lines highlight the disappearance of $Ag_3VO_2F_4$ peaks.

Experimental Section

Caution. Hydrofluoric acid is toxic and corrosive and must be handled with extreme caution and the appropriate protective gear! If contact with the liquid or vapor occurs, proper treatment procedures should be followed immediately.[27−29]

Materials. Ag_2O (99.5%, Fisher), V_2O_5 (99.6%, Alfa-Aesar), and aqueous hydrofluoric acid (48−50% HF by weight, Fisher) were used as received.

Synthesis. $Ag_4V_2O_6F_2$ was synthesized from a 4:1 molar ratio of Ag_2O:V_2O_5 in a $HF_{(aq)}$ solution. The silver oxide and vanadium oxide (0.3972 and 0.0779 g, respectively) were loaded into a HF-resistant reaction vessel (e.g., FEP Teflon pouch[30]) to which was added 1.6 g water followed by 0.2572 g of $HF_{(aq)}$. While the target phase begins to form nearly instantaneously, the solution was allowed to react for between 10 min and 72 h and filtered to recover $Ag_4V_2O_6F_2$.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were collected on a Rigaku XDS 2000 with Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å) and compared with patterns recorded in the JCPDS (Joint Committee of Powder Diffraction Standards) database.

---

(15) Bertoni, M. I.; Kidner, N. J.; Mason, T. O.; Albrecht, T. A.; Sorensen, E. M.; Poeppelmeier, K. R. *J. Electroceram.* **2007**, *18*, 189–195.

(16) Sorensen, E. M.; Izumi, H. K.; Vaughey, J. T.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2005**, *127*, 6347–6352.

(17) Marschilok, A. C.; Takeuchi, K. J.; Takeuchi, E. S. *Electrochem. Solid-State Lett.* **2009**, *12*, A5–A9.

(18) Sauvage, F.; Bodenez, V.; Vezin, H.; Albrecht, T. A.; Tarascon, J.-M.; Poeppelmeier Kenneth, R. *Inorg. Chem.* **2008**, *47*, 8464–8472.

(19) Bervas, M.; Mansour, A. N.; Yoon, W. S.; Al-Sharab, J. F.; Badway, F.; Cosandey, F.; Klein, L. C.; Amatucci, G. G. *J. Electrochem. Soc.* **2006**, *153*, A799–A808.

(20) Badway, F.; Mansour, A. N.; Pereira, N.; Al-Sharab, J. F.; Cosandey, F.; Plitz, I.; Amatucci, G. G. *Chem. Mater.* **2007**, *19*, 4129–4141.

(21) Palacin, M. R.; Amatucci, G. G.; Anne, M.; Chabre, Y.; Seguin, L.; Strobel, P.; Tarascon, J. M.; Vaughan, G. *J. Power Sources* **1999**, *81−82*, 627–631.

(22) Choi, W.; Manthiram, A. *J. Electrochem. Soc.* **2007**, *154*, A614–A618.

(23) Barker, J.; Saidi, M. Y.; Swoyer, J. L. *J. Electrochem. Soc.* **2003**, *150*, A1394–A1398.

(24) Ellis, B. L.; Makahnouk, W. R. M.; Makimura, Y.; Toghill, K.; Nazar, L. F. *Nat. Mater.* **2007**, *6*, 749–753.

(25) Albrecht, T. A.; Sauvage, F.; Poeppelmeier, K. R. US Provisional Patent 60/934,148, June 11, **2007**.

(26) The new compound of general formula $Ag_2VO_2F_4$ crystallizes in a monoclinic cell within $P2_1/n$ space group with $a = 5.772(2)$ Å, $b = 5.786(2)$ Å, $c = 8.102(2)$ Å, and $\beta = 90.576(2)°$ and exhibits a crystal structure density of 5.923 g/cm^3. $Ag_3VO_2F_4$ displays a cryolite-type structure, which is related to the perovskite structure, with corner sharing $[AgO_{2/2}F_{4/2}]^{3-}$ and $[VO_{2/2}F_{4/2}]^{+}$ octahedral and Ag^+ in the A-sites. A complete structural solution will be presented elsewhere.

(27) Bertolini, J. C. *J. Emerg. Med.* **1992**, *10*, 163–168.

(28) Peters, D.; Miethchen, R. *J. Fluorine Chem.* **1996**, *79*, 161–165.

(29) Segal, E. B. *Chem. Health Saf.* **2000**, *7*, 18–23.

(30) Harrison, W. T. A.; Nenoff, T. M.; Gier, T. E.; Stucky, G. D. *Inorg. Chem.* **1993**, *32*, 2437–2441.

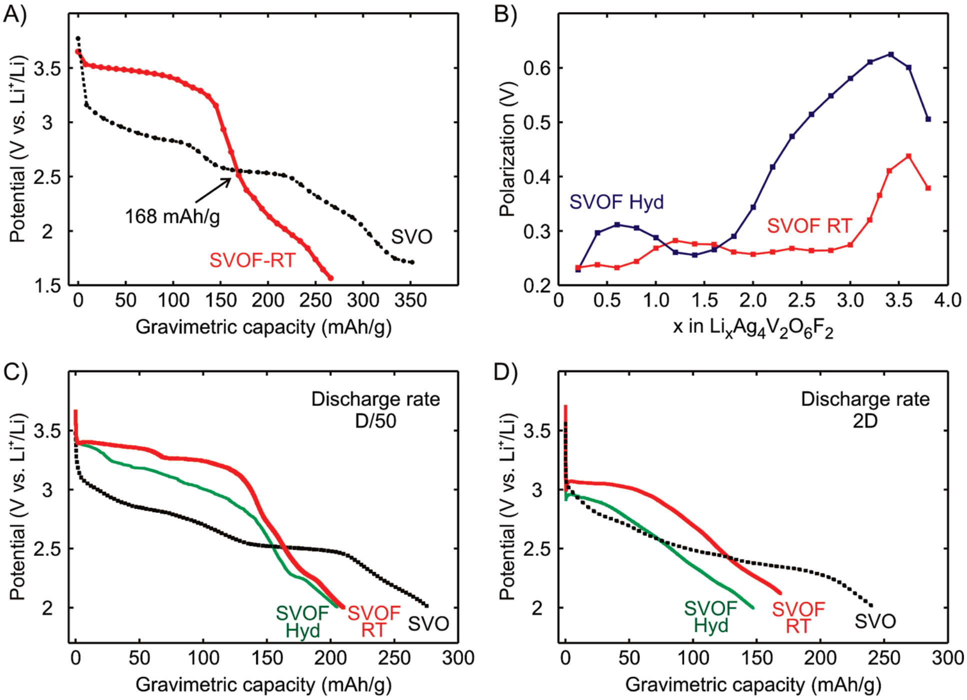

Figure 3. Potential vs gravimetric capacity curves comparing the discharge of $Ag_4V_2O_6F_2$ tailored at room temperature (SVOF-RT) and hydrothermal conditions (SVOF-Hyd) and $Ag_2V_4O_{11}$ (SVO) from hydrothermal conditions using galvanostatic intermittent titration technique (GITT) showing (a) SVOF and ε-SVO open circuit voltage and (b) the evolution of electrode polarization for SVOF-Hyd and SVOF-RT and a constant current discharge of all three materials at rates of (c) *D*/50 and (d) 2*D*.

Results and Discussion

Solution synthesis of silver vanadates has been studied for over a century at both elevated and room temperatures.[31–34] The appeal of such low-temperature (< 100 °C) approaches and draw for continued development of SVOF led to the exploration of the Ag_2O/V_2O_5 system in various concentrations of $HF_{(aq)}$. It was hypothesized that $Ag_4V_2O_6F_2$ would form from reactions with more dilute $HF_{(aq)}$ owing to the nature of the system studied at hydrothermal conditions.[16,30,35–37] Indeed, SVOF was one of the phases formed at room temperature from a molar reactant ratio of 4:1:15:x Ag_2O:V_2O_5:HF:H_2O, where $x = 180$ to form $Ag_4V_2O_6F_2$ and $x = 17$ to form the new $Ag_3VO_2F_4$. A 4:1 Ag_2O:V_2O_5 ratio is needed owing to the higher relative solubility of silver.[38,39] The minimum value of x is 17 due to the concentration of the $HF_{(aq)}$ stock solution of 48−50% HF by weight that gives a pH ~ 4, and a value of $x = 180$ corresponds to a concentration of 7% $HF_{(aq)}$. Figure 2 shows a series of powder X-ray diffractograms of the product from reactions with various acid concentrations. While using 48−50% $HF_{(aq)}$ gives rise to the new silver dense oxide fluoride $Ag_3VO_2F_4$, a HF concentration decreased to 33% allows formation of $Ag_4V_2O_6F_2$ alongside $Ag_3VO_2F_4$. By a concentration of 7%, $Ag_4V_2O_6F_2$ is formed without $Ag_3VO_2F_4$ as a secondary phase while the pH of the solution becomes neutral (6 < pH < 7). That is, additional water hydrolyzes $Ag_3VO_2F_4$ to give $Ag_4V_2O_6F_2$. The particle sizes of SVOF-RT, as determined by SEM, were 0.5 to 1 μm (Figure 1b). Yield was affected by variations on the reaction time and $HF_{(aq)}$ concentration (i.e., adjusting x). Specifically, a reaction time from 10 min to 72 h increased the yield of SVOF-RT based on silver from 4% to 16%, where the longer reaction times encourage further nucleation rather than particle growth and the majority of the product was precipitated in about 1 h.

To evaluate the electrochemical performance of SVOF-RT, it was compared to hydrothermally made ε-SVO[35] and SVOF.[16,36] This route for ε-SVO preparation yields nanosized flat needle-like particles of 150−400 nm wide, 1000 nm long, and 50 nm thick (Figure 1c). Similarly sized particles were recently highlighted to react vs lithium better than the standard product obtained by a solid state reaction, which gave an improved discharge rate capability.[12,40] We also report the performance of hydrothermally made $Ag_4V_2O_6F_2$ (SVOF-Hyd) particles to demonstrate the benefits of the reduced particle sizes of SVOF-RT. Electrochemical cells were prepared with an electrolyte of 1 M $LiPF_6$ in 1:1 EC/DMC.

---

(31) Britton, H. T. S.; Robinson, R. A. *J. Chem. Soc., Abstr.* **1930**, 2328–2343.
(32) Shivahare, G. C. *J. Inorg. Nucl. Chem.* **1966**, *28*, 657–658.
(33) Souchay, P.; Carpeni, G. *Bull. soc. chim.* **1946**, 160–168.
(34) Edgar, G. *Am. Chem. J.* **1911**, *44*, 467–472.
(35) Albrecht, T. A.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2007**, *46*, 1704–1708.
(36) Izumi, H. K.; Sorensen, E. M.; Vaughey, J. T.; Poeppelmeier, K. R. U.S. Provisional Patent 60/606,475, September 1, **2004**.
(37) Sheets, W. C.; Mugnier, E.; Barnabe, A.; Marks, T. J.; Poeppelmeier, K. R. *Chem. Mater.* **2006**, *18*, 7–20.
(38) Thomas, H. J.; Jache, A. W. *J. Inorg. Nucl. Chem.* **1960**, *13*, 54–57.
(39) Nikolaev, N. S.; Buslaev, Y. A. *Khim. Redk. Elem.* **1955**, 57–63.
(40) Takeuchi, E. S.; Leising, R. A.; Hong, G.; Rubino, R. U.S. Patent Application 2004-185346, September 23, 2004.

The galvanostatic intermittent titration technique (GITT) was used to evaluate the polarization difference between the three materials. Cells were discharged at a rate of $D/10$ (i.e., 1 lithium ion inserted in 10 h) followed by a relaxation for 20 h to restore the cathode to an equilibrium state. The polarization evolution is defined herein as being the potential difference between equilibrium and under-current states. Figure 3a shows the thermodynamic discharge curves for SVOF and ε-SVO, highlighting the higher potential for SVOF for the first 168 mAh/g owing to the higher content of silver in the phase and the presence of partial F^- coordinating silver.[16,36] Also evaluated was the difference in polarization between SVOF materials synthesized from hydrothermal and room temperature conditions (Figure 3b). SVOF-RT exhibits a relatively constant polarization of ~0.25 V for the first 3 Li^+ inserted, and up to a maximum of 0.44 V at ~3.5 Li^+, whereas the overpotential of SVOF-Hyd increases from 0.3 to 0.63 V between 1.5 and 3.5 Li^+ inserted. This decrease in overpotential, indicative of relieved kinetic barriers during the displacement and reduction of silver, results from the decreased particle sizes that provide a shorter ion diffusion length inward from the particle edge.[18]

Using a low cathodic current equivalent to a $D/50$ discharge rate (i.e., 1 lithium ion inserted in 50 h), SVOF-RT is capable of an uptake of lithium at up to ~450 mV higher than the nanosized ε-SVO for the first 163 mAh/g delivered (Figure 3c). This is followed by a threshold at which the cell potential monotonously drops owing to the change from Ag^+ to V^{5+} reduction.[18] At this low discharge rate, SVOF-Hyd performs comparably to SVOF-RT in terms of capacity. Using a discharge rate of $2D$ (i.e., 1 lithium ion inserted in 30 min), the advantages of using SVOF-RT are maintained despite a closer potential gap between this material and SVO (~200 mV for the first 113 mAh/g) (Figure 3d). This smaller gap in potentials is a result from the higher ionic limitations in the SVOF Ag^+/Li^+ displacement reaction caused by the less well-defined ionic pathways in the structure for the silver ion to withdraw.[18] Unlike at the low discharge rate, SVOF-RT exhibits superior discharge properties versus SVOF-Hyd at high rates, further emphasizing the importance of particle size.

Numerous electrochemical Swagelok-type cells composed of a similar cathode loading (~20 mg active material on a ~1.23 cm^2 electrode surface) were discharged at different rates between $D/50$ to $2D$. The energy density vs power density of each material is gathered in a Ragone chart with cutoff points of (a) 3 V and (b) 2.5 V, below which ICDs start to operate with less efficiency (Figure 4). The space domains in the figure were obtained by the repetition of multiple experiments. As a result, two features can be concluded: (i) the decrease of $Ag_4V_2O_6F_2$ particle size by 1 order of magnitude is beneficial for an increase of both power density and energy density and (ii) SVOF-RT compares favorably with nanosized ε-SVO synthesized from hydrothermal conditions.

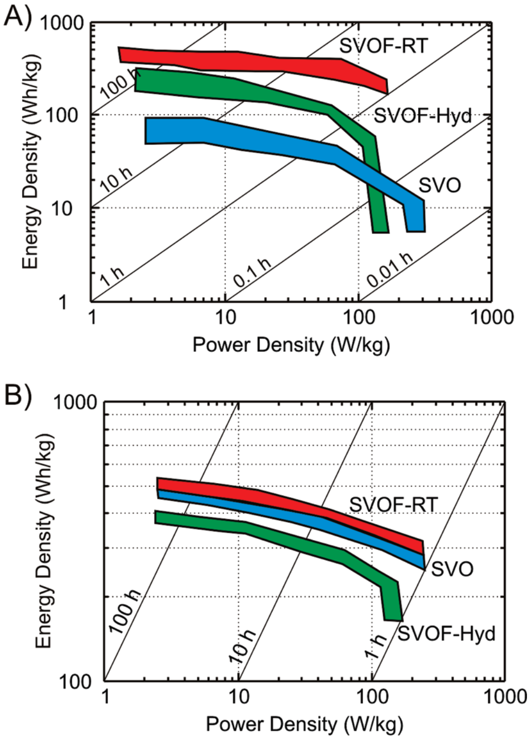

Figure 4. Ragone chart comparing energy density vs power density of cathodes consisting of $Ag_4V_2O_6F_2$ synthesized at room temperature (SVOF-RT) and at hydrothermal conditions (SVOF-Hyd) and nanosized $Ag_2V_4O_{11}$, for potentials above 3 and 2.5 V.

Conclusion

Investigation of the $Ag_2O-V_2O_5-HF-H_2O$ system with a Ag:V molar reactant ratio of 4:1 at room temperature has led to the realization of new strategies on low temperature synthesis. Notably unique is the reaction of silver vanadium oxide fluoride, $Ag_3VO_2F_4$, with water and preparation of the cathode material $Ag_4V_2O_6F_2$ that shows enhanced electrochemical behavior owing to the smaller particle sizes.[41] This room temperature synthetic route has multiple advantages, a straightforward experimental procedure, and a rapid synthesis (~1 h) without complex apparatus, and it represents a step toward a more energy efficient solid state chemistry. Ongoing efforts are underway to transfer such diverse room-temperature chemistry to decrease particle size further, to control specific shape, and to find other nonvanadium-based cathode materials.

Acknowledgment. This work was supported from the Office of Naval Research (MURI Grant N00014-07-1-0620) and the National Science Foundation (Solid State Chemistry Awards No. DMR-0604454), and the use of the Central Facilities was supported by the MRSEC program of the National Science Foundation (DMR-0520513).

Supporting Information Available: Description and figures for powder X-ray diffraction refinement and TEM on postelectrochemical discharge of $Ag_4V_2O_6F_2$ (PDF); a video of the synthesis at 20× speed (AVI). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(41) In addition, we have studied the electrochemical behavior of $Ag_3VO_2F_4$. These experiments showed this material to be unstable within the electrolyte and thus exhibit a rapid potential drop upon discharge.