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Atypical $\text{Li}_{1.1}\text{V}_3\text{O}_8$ Prepared by a Novel Synthesis Route

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This work deals with a new sol-gel route named complex sol-gel process (CSGP) based on a very strong complexing agent (ascorbic acid) to synthesize gel precursors of $\text{Li}_{1.1}\text{V}_3\text{O}_8$. Results show that original morphologies are stabilized for anhydrous samples prepared by annealing these gels at low temperature. They lead to either high capacity and unexpected excellent cyclability, or atypical lithium insertion behavior.

Lithium vanadium oxide, $\text{Li}_{1+\alpha}\text{V}_3\text{O}_8$ ($\alpha \approx 0.1-0.2$), has been intensively studied for the past 20 years for its attractive electrochemical properties. Indeed, it provides a fair energy density and a good capacity retention. $\text{Li}_{1+\alpha}\text{V}_3\text{O}_8$ could be prepared by several routes. One interesting synthesis technique consisted in the annealing at temperatures higher than 300°C of a gel precursor obtained from the reaction of V_2O_5 and $\text{LiOH}\cdot\text{H}_2\text{O}$ at 50°C under N_2 .¹⁻³ Such a technique allows for obtaining a sample with an initial specific capacity close to theory but with a poor cyclability.³⁻⁵ In a previous work,⁴ cyclability was found to be dependent on morphology of the grains. Such results incited us to search for new synthesis routes leading to unusual morphologies with the aim to increase cyclability of low-temperature prepared samples.

The goal of this work was to evaluate the interest of the new variant sol-gel route named complex sol-gel process (CSGP) developed by Deptuła et al.⁶ to synthesize gel precursors of $\text{Li}_{1.1}\text{V}_3\text{O}_8$. The main feature in this process is the use of a very strong complexing agent (ascorbic acid, ASC) for the sol preparation. Such procedure was successfully applied to the synthesis of $\text{Li}_x\text{Mn}_2\text{O}_{4\pm\delta}$ spinels,^{6,7} $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ layered oxides,^{8,9} and composite $\text{TiO}_2\text{-LiCoO}_2$.¹⁰

We present here results of synthesis, characterization, and lithium insertion behavior of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ samples prepared by annealing CSGP gels at low temperature. Results show unusual morphologies leading to excellent cycling behavior, as well as an original Li insertion behavior.

Experimental

A flowchart of the preparation procedure is shown in Fig. 1. Commercial NH_4VO_3 was dissolved at 80°C in water and immediately introduced into the reservoir of a Rotavapor equipment (Büchi, Switzerland) after addition of ascorbic acid (ASC). Concentrated LiOH was then slowly added into the reservoir. A chemical treatment of the sample with concentrated HNO_3 and H_2O_2 (1 mL of each reagents on 1 g of powder) was also applied in order to remove traces of ASC in the sample. The obtained slurry was then dried at 105°C for 24 h. The sample is noted as ASCR_{105} .

The previous process was repeated once without addition of ASC (sample noted noASC_{105}) and once without chemical treatment (sample noted ASC_{105}), everything else being the same. All samples were heat-treated at 400°C for 6 h before electrochemical studies (obtained samples are noted ASCR_{400} , noASC_{400} , and ASC_{400} , respectively).

For the sake of comparison, another sample prepared by the standard sol gel route ($\text{V}_2\text{O}_5 + \text{LiOH}\cdot\text{H}_2\text{O}$) and annealed at 400°C, noted SG_{400} , was also investigated.

All thermal treatments were performed in an air-ambient-programmed Carbolite furnace type CSF 1200. Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) in

the attenuated total reflectance (ATR) mode and FT-Raman measurements were performed on a Setaram TG-DSC 111, a Bruker Vertex 70, and a Bruker RFS 100 ($\lambda = 1064$ nm), respectively.

X-ray diffraction (XRD) data were collected ($\lambda_{\text{CuK}\alpha}$) with a $\Theta/2\Theta$ Bruker D5000 diffractometer mounted with a linear MOX-TEK detector.

Scanning electron microscopy (SEM) images were obtained from a GEOL 6400 microscope. Electrochemical measurements were achieved with a Mac-Pile controller using two-electrode Swagelok-type cells. The composite electrode was coated on an Al disk from a mix of 85% of $\text{Li}_{1.1}\text{V}_3\text{O}_8$, 10% of C Super P, and 5% of polyvinylidene fluoride (PVDF). Ethylene carbonate:dimethyl carbonate (EC:DMC)(2:1) + 1 M LiPF_6 (from Merck) was used as the electrolyte. Galvanostatic cycling was performed using a current that corresponds to the insertion-desinsertion of 1 Li within 2.5 h and 1 Li within 5 h per formula unit, respectively (~ 60 mA/g, ~ 0.3 mA/cm²) in the range 3.7 to 2 V.

Results and Discussion

TGA measurements (10 K/min) show that all samples are water-free above 350 to 450°C. ASC_{105} is the only sample that presents an increasing weight above 500°C, which can be attributed to oxidation of V^{IV} species. The weight increase roughly corresponds to oxidation of all V^{IV} to V^{V} with the addition of near to 1.5 atoms of oxygen per formula unit, leading to $\text{Li}_{1.1}\text{V}_3\text{O}_8$. It means that only the ASC_{105} sample contains mainly V^{IV} species.

Infrared measurements show typical $\text{V}=\text{O}$, $\text{V}-\text{O}-\text{V}$, and $\text{Li}-\text{O}-\text{V}$ vibrations of vanadium oxide compounds for samples fired at 400°C and do not show any trace of remaining carbonates coming from thermal decomposition of the organic-based precursor. Raman spectra did not show any carbon traces in the 400°C samples. These results indicate that all 400°C samples are organic and carbon-free. Figure 2 presents XRD patterns of these four samples. As deduced from Rietveld refinement, unit cell parameters for $\text{Li}_{1.1}\text{V}_3\text{O}_8$ are similar for all samples and ASCR_{400} shows a strong preferred orientation owing to the platelet-like shape of the grains (see below). Note also that all samples prepared from heat-treatment of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ gels prepared using CSGP method show traces of $\beta\text{-Li}_{0.3}\text{V}_2\text{O}_5$ (β)¹¹ (5 wt % for ASC_{400} , roughly 2 wt % for noASC_{400} , and a negligible amount for ASCR_{400}). ASCR_{400} contains in addition traces of V_2O_5 (*).

The SEM study is summarized on Fig. 3. The phase impurities detected by XRD were not seen as separated grains in the SEM images of corresponding samples. noASC_{400} sample displays a morphology close to that observed for standard $\text{Li}_{1.1}\text{V}_3\text{O}_8$ SG_{400} , whereas the ASC_{400} sample shows large (about 30 μm) porous polycrystalline grains and the ASCR_{400} sample is made of large (about 3×6 μm) well-crystallized platelets. Such morphologies have never been observed before for low-temperature $\text{Li}_{1.1}\text{V}_3\text{O}_8$ to our knowledge, as submicrometer size agglomerates of needle-like grains are obtained using standard synthesis procedures.⁴ It should

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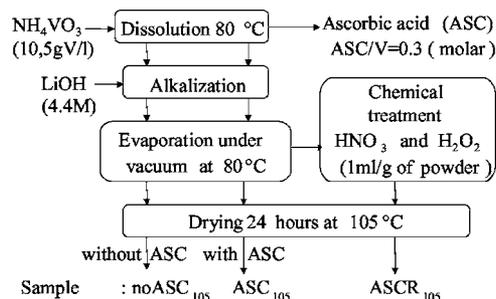


Figure 1. Flowchart for preparation of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ gels using CSGP method.

be concluded then, that our CSGP routes, including the chemical treatment that lead to the ASCR sample, are very efficient in providing new morphologies of $\text{Li}_{1.1}\text{V}_3\text{O}_8$. Consequences are now discussed in respect to electrochemical performance.

Figure 4 shows the capacity retention on cycling of the four samples. Although initial capacity of SG_{400} , ASC_{400} , and ASCR_{400} are similar and close to 245 mAh/g, the capacity retention of the two latter looks much better, especially for ASC_{400} (capacity loss $\sim <0.3\%$ /cycle), than that of standard SG_{400} . Good cycling behaviors (capacity loss $<0.5\%$ /cycle) of low temperature $\text{Li}_{1.1}\text{V}_3\text{O}_8$ samples have been obtained using either very specific experimental conditions (50 wt % of graphite in the positive electrode mixture,¹² potentiostatic equilibration upon each oxidation,¹³) or pillaring molecules.^{14,15} It should also be noted that, to our best knowledge, other works where the active material has been prepared at 400°C or lower and tested under similar experimental conditions to those reported here show a poorer capacity retention (loss $> 1.5\%$) on cycling.^{4,16} In this respect, our recent results show that this poor capacity retention was confirmed irrespective of the liquid electrolyte (solvents and salts), the cell type that was used (Swagelok, button, or coffee bags) or the positive electrode preparation procedure including the very promising one proposed by Guy et al.¹⁷ Moreover, we observe that the capacity retention is strongly improved upon increasing the cycling discharge rate by a factor 2.5 (as in Ref. 18) or more or by using solid electrolyte poly(ethylene oxide).¹⁹ For these reasons we believe that the capacity retention of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ mainly depends on side reactions (or their consequences) such as the formation of an inorganic-organic layer on the surface of the grains that occurs on cycling with liquid electrolytes.¹⁹ On this basis the larger grains for ASCR_{400} and especially the specific mor-

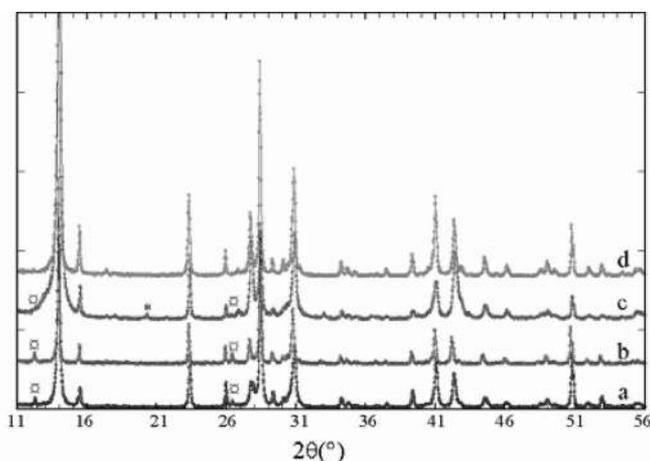


Figure 2. XRD patterns of (a) noASC_{400} , (b) ASC_{400} , (c) ASCR_{400} , and (d) SG_{400} samples. Lines that corresponds to $\beta\text{-Li}_{0.3}\text{V}_2\text{O}_5$ and V_2O_5 are noted (□) and (*), respectively.

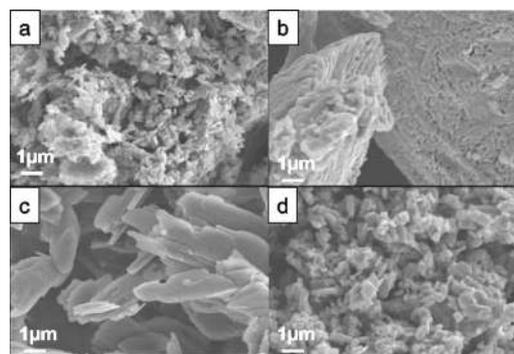


Figure 3. SEM pictures of (a) noASC_{400} , (b) ASC_{400} , (c) ASCR_{400} , and (d) SG_{400} samples.

phology for ASC obtained at low temperature open interesting prospects for optimizing the cycling properties of this compound without strong capacity loss.⁴ This effect was also observed recently by Gao et al.²⁰ who obtained a higher initial capacity (350 mAh/g), although the capacity loss was larger ($\sim 1.5\%$ /cycle).

Very surprisingly, the noASC_{400} sample presents a very low initial capacity, although it has a similar grain size as standard SG_{400} . Such behavior was reproducible. It has not been obtained previously to our knowledge and is totally unexpected. The incremental capacity curves vs voltage on the first cycle are shown on Fig. 5 for each sample. No peaks related to V_2O_5 are observed for sample ASCR_{400} showing that V_2O_5 content in the sample is low. Note that in the case of ASC_{400} the reduced phase $\beta\text{-Li}_{0.3}\text{V}_2\text{O}_5$ is active and responsible for the small peaks observed at roughly 3.45 and 3.65 V on oxidation.²¹ One main difference between noASC_{400} and other samples is the very low amplitude of the 2.6 V process as well as the absence of that at 2.2 V in the former. The process at 2.6 V appears in other samples as a single or a double peak in the 2.4-2.5 V range on the first discharge, and a single peak at 2.7 V on the first charge. This electrochemical process is related to the phase transformation between $\text{Li}_{-3}\text{V}_3\text{O}_8$ and $\text{Li}_4\text{V}_3\text{O}_8$ ²² and corresponds roughly to 90 mAh/g. The low amplitude of the phase transformation has been confirmed by XRD of a noASC_{400} sample at the end of the first discharge and accounts for the low capacity recovered on discharge. Such phenomenon has never been observed yet on various $\text{Li}_{1.1}\text{V}_3\text{O}_8$ samples studied in our laboratory and is very surprising. Further work on thorough characterization of noASC_{400} sample is under way in order to assess the origin of the absence of this phase transformation.

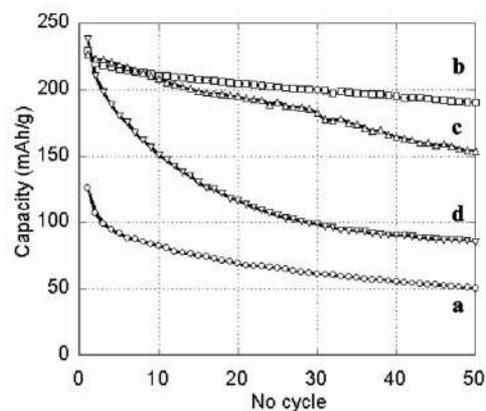


Figure 4. Variation of specific capacity recorded during galvanostatic cycling for (a) noASC_{400} , (b) ASC_{400} , (c) ASCR_{400} , and (d) SG_{400} .

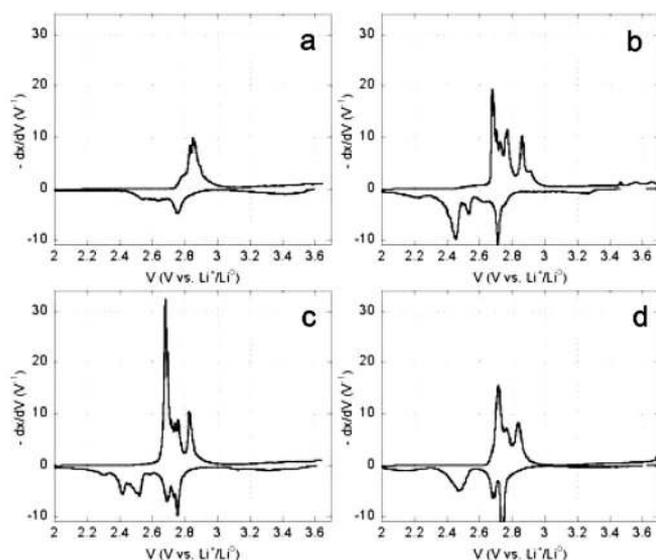


Figure 5. Incremental capacity vs voltage curves, obtained from galvanostatic cycling data for (a) noASC₄₀₀, (b) ASC₄₀₀, (c) ASCR₄₀₀, and (d) SG₄₀₀ samples.

Conclusions

The preparation of anhydrous Li_{1.1}V₃O₈ through the original CSGP process and variants gives rise to unexpected Li insertion behavior.

One sample shows atypical Li insertion process with no Li_{1.3}V₃O₈ to Li_{1.4}V₃O₈ phase transformation. It is detrimental to the delivered capacity, but it opens new and interesting issues in the field of the basic understanding of Li_{1.1}V₃O₈ Li insertion behavior. Further work is needed in order to assess the origin of the absence of the phase transformation.

Some samples display improved cycling behavior compared to standard low temperature Li_{1.1}V₃O₈, which seems related to their unusual morphology. Such a finding leads to new directions for optimizing the cycling properties of these compounds. Especially, variations around the routes investigated here appear as extremely promising for preparation of even better performing samples.

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