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Ionic-Liquid-Assisted Synthesis of Nanostructured and Carbon-Coated Li₃V₂(PO₄)₃ for High-Power Electrochemical Storage Devices

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Carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) displaying nanostructured morphology can be easily prepared by using ionic-liquid-assisted sol-gel synthesis. The selection of highly viscous and thermally stable ionic liquids might promote the formation of nanostructures during the sol-gel synthesis. The presence of these structures shortens the diffusion paths and enlarges the contact area between the active material and the electrolyte; this leads to a significant improvement in lithium-ion diffusion. At the same time, the use of ionic liquids has a positive influence on the coating of the LVP particles, which improves the electronic

Introduction

Rechargeable lithium-ion batteries (LIBs) have been extensively developed as promising energy-storage devices for electric and hybrid electric vehicles and as intermittent renewable energy sources owing to their high energy, power densities, and long cycle lifetimes.^[1-3] Recently, lithiated transition-metal phosphates, such as LiMPO₄ (M=Mn, Fe, Co, Ni) and Li₃M₂(PO₄)₃ (M=Ti, V, Fe), have attracted great interest as potential cathode materials for LIBs, because they have good electrochemical and thermal stabilities, competitive energy density, and high operating potentials.^[4-7]

Among the compounds tested so far, lithium vanadium phosphate, $Li_3V_2(PO_4)_3$ (LVP), which consists of a 3D framework of slightly distorted VO₆ octahedra and PO₄ tetrahedra that share oxygen vertexes hosting lithium ions in relatively large interstitial sites, offers the optimal combination of high operating voltage, high specific capacity, good ion mobility, and excellent thermal stability.^[8–13] LVP can theoretically reversibly deliver $3Li^+$ ions per formula unit within a potential range from 3.0 to 4.8 V versus Li/Li^+ , which results in a maximum discharge capacity of 197 mA h g⁻¹. In the potential range between 3.0 and 4.3 V, based on the V³⁺/V⁴⁺ redox couple, a re-

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conductivity of this material; this leads to enhanced chargetransfer properties. At a high current density of 40 C, the LVP/ *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide material delivered a reversible capacity of approximately 100 mA hg⁻¹, and approximately 99% of the initial capacity value was retained even after 100 cycles at 50 C. The excellent high rate and cycling stability performance make Li₃V₂(PO₄)₃ prepared by ionic-liquid-assisted sol–gel synthesis a very promising cathode material for high-power electrochemical storage devices.

versible capacity of 133 mA $h\,g^{-1}$ can still be obtained. $^{[9]}$ LVP exhibits good ionic conductivity, because it features a 3D path created by PO₄³⁻ units that allows fast lithium-ion migration in three dimensions.^[10] However, LVP displays intrinsic low electronic conductivity (i.e., $2.4 \times 10^{-7} \,\text{S}\,\text{cm}^{-1}$ at room temperature),^[14] which limits its application in LIBs, especially for cases in which the rate performance is an important prerequisite.^[11-13] In the past few years, various synthesis and processing approaches have been employed to solve this problem. Carbon coating is presently regarded as an effective way to improve the performance of LVP. However, it is rather difficult to homogeneously encapsulate LVP with a carbon shell during the formation processes that are performed at high temperatures.^[15-17] Also, an excess amount of carbon might decrease the filling density of active substances in the cathodes. Finally, it is also rather challenging to realize an optimal mixture of carbon and LVP particles. If the contact area between the carbon particles and the LVP material is inhomogeneous, a decrease in charge/discharge capacity will be observed.[11-13] Considering the above-mentioned points, the realization of an effective carbon coating for LVP particles appears guite challenging. Nevertheless, taking into account the low electronic conductivity of this material, the optimization of such a coating appears to be a key factor in achieving a high discharge capacity and good cyclability, especially at higher current rates.

lonic liquids (ILs) are a family of unconventional molten salts with melting points below 100 °C. They are made of organic cations and anions, the choice and combination of which will affect not only their melting temperature but also their solvating properties.^[18,19] ILs are good solvents for a huge variety of organic and inorganic materials, and relative to traditional solvents, they offer many distinct advantages such as negligible

vapor pressure, non-flammability, and high chemical stability. Additionally, their low melting points (as low as -80 °C) and high thermal stability (up to 300 °C) provide a wide liquidus range for inorganic synthesis.^[18,19] Recently, it was shown that the morphology of cathode materials, such as LiFePO₄, can be varied through the application of different ILs as solvents in a process referred to as "ionothermal synthesis".^[20] Owing to these properties, ILs appear as unique synthetic media, and their use might lead to the realization of materials with morphologies and properties that are not possible by using conventional solvents and methods.^[21–23]

In this manuscript, we report the first use of the ILs N-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIMTFSI) in the IL-assisted synthesis of LVP as a cathode material. During the synthesis process, the ILs facilitate the preparation of samples with distinct morphologies as a result of the high thermal stability of the ILs. Furthermore, ILs are good precursors for carbon coatings because their fluidic properties allow them to permeate the surface of the particles, especially at increased temperatures, which occurs during the calcination steps.^[24] This behavior favors the formation of a thin uniform coating layer on the LVP particle surface and the realization of materials with extraordinary rate capability and cycling stability. These properties designate these LVP particles as a very promising cathode material for the development of advanced LIBs.

Results and Discussion

The two carbon-coated LVP/ILs were prepared by using the IL PYR₁₄TFSI (LVP/PYR₁₄TFSI) or EMIMTFSI (LVP/EMIMTFSI) as an additive in a sol–gel-based process. The raw materials V₂O₅, H₂C₂O₄•2 H₂O, NH₄H₂PO₄, and Li₂CO₃, were dissolved and mixed to form the precursor solutions. Afterwards, the IL was injected into the solution. To compare the LVP samples prepared by the IL-assisted synthesis with a conventionally carbon-coated material, a sample was prepared by adding sucrose (LVP/C) instead of the IL to the precursor solution. Moreover, a carbon-free (pure LVP) sample was prepared by using the same synthetic route.

During the preparation of all the samples, the precursor was initially dried (100 $^\circ\text{C})$ and then decomposed at 350 $^\circ\text{C}$ for 4 h under an argon atmosphere. Afterwards, the pre-calcined precursor was treated at 800 °C for 8 h under an argon atmosphere. Thermogravimetric analysis (TGA) results (see Figure S1, Supporting Information) indicated that the decomposition of both ILs occurred at nearly the same temperature, above 350 °C. Therefore, during the drying process at 100 °C no evaporation of the ILs took place, and both ILs were completely soaked into the precursor. At 350°C, both ILs were only partially decomposed, but in the second calcination step up to 800 °C the ILs decomposed completely to form a carbon-coating layer on the LVP particles. In the case of LVP/C, the situation was different. During the drying process, sucrose was dispersed onto (and not soaked into) the precursor. Given that sucrose is not stable above 200°C, it decomposed completely during the first calcination step up to 350 °C and started to form a carbon-coating layer on the LVP particles. Considering these differences, it is clear that the introduction of ILs during the synthesis might have a strong influence on the morphology as well as the carbon-coating of the LVP particles

The XRD patterns of the LVP samples are shown in Figure 1. For all samples, the intense diffraction peaks are indicative of a well-crystallized monoclinic phase within the *P*21/*n* space group. The weighted factors R_{wp} and R_p were below 15%, and therefore, Rietveld refinement was expected to give reliable results. The lattice parameters (noted in Table S1) are in good agreement with ICSD No. 96962. Furthermore, no carbon phase was detected in the XRD patterns of all the samples; this indicated that the carbon generated from both sucrose and the IL was amorphous and that its presence did not influence the crystal structure of the LVP.^[25]

The elemental composition obtained from CHN combustion analysis of the pure LVP, LVP/C, LVP/PYR₁₄TFSI, and LVP/ EMIMTFSI samples is shown in Table 1. According to the ele-

Table 1. Elemental analysis of the pure LVP, LVP/C, LVP/PYR14TFSI, and LVP/EMIMTFSI materials.							
Material Element [wt %]							
	2.04	0.16	1.15				
	2.04	0.16	1.15				
LVP/C	2.44	0.10	0.59				
pure LVP	0.06	0.08	0				

mental analysis results, the carbon content of LVP/PYR₁₄TFSI and LVP/EMIMTFSI was 2.04 and 2.66 wt%, respectively. The LVP/C sample showed a similar carbon content of 2.44 wt%. In contrast, pure LVP had a carbon content of only 0.06 wt% and was therefore practically not carbon-coated. All carbon-coated samples included a small fraction of nitrogen species, which originated from the decomposition of NH₄H₂PO₄.

The morphology of the as-prepared materials was examined by scanning electron microscopy (SEM, Figure 2). The pure LVP sample was found to consist of irregular particles with a size distribution of 1–2 μ m, and they agglomerate to form bulky particles (Figure 2a). LVP/C is made up of particles that are smaller than those of pure LVP. These particles display irregular morphology and shape, and a strong aggregation of small primary particles to bigger structures is clearly visible (Figure 2b). The LVP/EMIMTFSI sample displays irregular particles that are comparable in size to those of LVP/C. Furthermore, the small particles of this sample agglomerated into larger secondary particle structures as well (Figure 2c). In contrast to the other samples, LVP/PYR₁₄TFSI shows a very distinct morphology (Figure 2d and Figure S2). Although some particles are similar in size and morphology to the particles in the LVP/EMIMTFSI sample, a large fraction of the material grows into particles with a nanorod-like shape. These nanostructures, which are on average 50 nm thick and approximately 1 µm long, cover and interconnect the bigger particles. Several reports have indicat-

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Figure 1. Comparison of experimental XRD patterns of a) LVP/PYR₁₄TFSI, b) LVP/EMIMTFSI, c) LVP/C, and d) pure LVP with calculated patterns on the basis of the ideal structure of monoclinic LVP (ICSD No. 96962). The difference between observed and calculated diffraction data and the reflex positions are represented at the bottom of each pattern.

ed that the presence of residual carbon prevents the growth of large particles.^[26] This finding was confirmed by the SEM images of LVP/C and LVP/EMIMTFSI. Figure 2d clearly shows that the use of PYR14TFSI not only prevented the formation of large particles but also led to the formation of nanostructures that greatly shorten the diffusion and transport distance of the lithium ions and electrons compared to the other LVP samples. It is known that the morphology of samples obtained by solgel synthesis is influenced by the conditions of the gelation step. It was found that ILs are able to act as a template medium during the sol-gel synthesis to direct the growth of solids into distinct morphologies.^[27] The difference between PYR₁₄TFSI and EMIMTFSI is most likely their different solvent interactions that affect and promote the growth of either nanorod-like structures or particles.^[28] Given that the two ILs display comparable thermal stability, it is reasonable to suppose that the formation of nanorod-like structures in LVP/PYR14TFSI is also affected by the much higher viscosity of PYR₁₄TFSI (63 cP) relative to that of EMIMTFSI (28 cP).^[29,30] Considering these results, it appears that the presence of a highly viscous and thermally stable media, such as PYR₁₄TFSI, might promote the formation of nanostructure materials during the sol-gel synthesis.

a single spot hardly represent a macroscopic sample, the collection of several spectra provides more reliable information. The Raman spectra show D and G bands at 1350 and 1590 cm⁻¹, respectively. The G band corresponds to the optically allowed E_{2q} zone center mode of crystalline graphite and the D band is connected with the disorder-allowed zone-edge mode of graphite. As shown in the figure, in the spectra recorded for LVP/C, LVP/PYR14TFSI, and LVP/EMIMTFSI, a strong D band and a slightly weaker G band are observed,^[31] this indicates that PYR₁₄TFSI and EMIMTFSI are able to provide a homogenous carbon-coating layer that is comparable to glucose. The ratio of the D and G bands indicates that the coating layer is dominated by disordered carbonaceous materials but that it also includes a significant amount of graphitic carbon. The pure LVP powder shows no clear band in this region, which is in line with its extremely low carbon content. However, pure LVP shows strong bands that originate from intermolecular stretching vibrations of the PO4³⁻ anion.^[32] These bands are found at 927, 975, 1007, 1029, and 1058 cm⁻¹. Some of these

Figure 3 shows the spectra obtained by averaging the

Raman data collected from a 5×5 pattern in an area of $25 \times$

25 µm of the pristine powders. Although the Raman spectra of



Figure 2. SEM images of a) pure LVP, b) LVP/C, c) LVP/EMIMTFSI, and d) LVP/PYR14TFSI.



Figure 3. Raman spectra of the four different samples: LVP/PYR₁₄TFSI, LVP/ EMIMTFSI, LVP/C, and pure LVP.

signals are also observed in the spectra of the carbon-coated materials but with strongly reduced intensities. The occurrence of the bands originating from the PO_4^{3-} anion indicates a non-uniform carbon coating. However, the extremely low intensities together with the fact that these spectra represent a 25 × 25 µm area of sample show that the carbon-coating layer is almost omnipresent.

To evaluate the properties of the LVP surface in more detail, X-ray photoelectron spectroscopy (XPS) study on all four prepared materials was undertaken. In all samples, the binding energy of the main peak at 517.4 eV $(2p_{3/2})$ is similar to the binding energies reported for LVP, which confirms the V³⁺ oxidation state,^[32,33] and the presence of a second peak at 524.7 eV $(2p_{1/2})$ indicates the spin–orbit splitting of the V2p orbital (Figure S3). Table 1 illustrates the elements that are found in the upper surface layer in an area of $300 \times 700 \,\mu$ m of the asprepared LVP samples. All four samples show a high amount of oxygen that originates from surface groups of the carbon coating and the phosphate anions of the LVP as well. However, the pure LVP sample displays an oxygen fraction of 53%, whereas the carbon-coated samples show a fraction of approximately 40%. The carbon coating reduces the amount of oxygen atoms in the surface layer significantly. The pure LVP sample contains, according to CHN elemental analysis, only 0.06 wt% carbon. The XPS data show that the amount of carbon on the surface is approximately 25%, but in the other carbon-coated samples, approximately 40% of carbon is detected. A large fraction of this carbon can be attributed to adventitious carbon. Furthermore, this illustrates that most carbon in the sample will aggregate on

the surface of the material. The same is true for nitrogen, which was detected in the CHN analysis ($\approx 1 \text{ wt \%}$) of the carbon-coated materials, and it is also found on the surface in an atom fraction of 2–3% (Table 2). In addition to these ele-

Table 2. Elemental composition of the surface of the pure LVP, LVP/C, LVP/PYR ₁₄ TFSI, and LVP/EMIMTFSI materials.									
Material	Elemen O	t [at %] V	N	с	S	Р			
LVP/PYR ₁₄ TFSI LVP/EMIMTFSI LVP/C pure LVP	43.9 40.5 40.4 53.0	4.2 4.6 4.9 4.7	2.8 2.3 2.2 0.5	37.2 40.1 37.2 24.7	0.0 0.5 0.0 0.0	11.9 12.2 15.3 17.0			

ments contained in the active LVP material, sulfur was detected in a very low fraction in the LVP/EMIMTFSI sample. This trace amount of sulfur on the surface of the material may hint to incomplete decomposition of the TFSI anion. This small trace and the absence of any sulfur in the LVP/PYR₁₄TFSI material show that the decomposition of the IL during the calcination steps up to 800 °C was very effective.

After the structural and morphological characterization, the electrochemical properties of pure LVP, LVP/C, LVP/PYR₁₄TFSI, and LVP/EMIMTFSI were investigated. Figure 4a shows the cyclic voltammetry (CV) curves of the composite electrodes containing the above-mentioned LVP samples, as obtained at a scan rate of 0.05 mV s^{-1} in the potential range from 3.0 to 4.3 V (vs. Li/Li⁺) at 20 °C. As shown, all electrodes present three couples of oxidation and reduction peaks between 3.0 and



Figure 4. a) Comparison of the cyclic voltammograms of the pure LVP, LVP/C, LVP/EMIMTFSI, and LVP/PYR₁₄TFSI electrodes at a scan rate of 0.05 mV s⁻¹ in a potential range from 3.0 to 4.3 V. b) Cyclic voltammetry curves and c) the linear relationship of the peak current (i_p) versus the square root of the scan rate ($v^{1/2}$) for LVP/PYR₁₄TFSI at various scanning rates between 3.0 and 4.3 V. d) Comparison of the diffusion coefficients (for oxidation and reduction) of the four different materials at peak positions a, b, and c.

4.3 V. The first two anodic peaks correspond to the extraction of the first Li⁺ ions over two steps, which suggests the formation of $Li_{2,5}V_2(PO_4)_3$ and $Li_2V_2(PO_4)_3$, whereas the second Li^+ ion is removed through a single step corresponding to the third anodic peak at 4.10 V. The three cathodic peaks are attributed to reinsertion of the two Li⁺ ions into the host lattice, which is accompanied by the V^{4+}/V^{3+} redox reaction.^[26] Even though all samples show the typical profile of LVP, the peaks of LVP/C and LVP/IL are much sharper and symmetrical than those of pure LVP. This difference is clearly related to the difference in the electronic conductivity of these samples and is indicative of the importance of the carbon coating for the realization of high-performance LVP-based electrodes. Among the carboncoated samples, the two LVP/IL materials display a lower potential difference between the anodic and corresponding cathodic peaks than LVP/C; this is indicative of a higher reversibility for the charge-discharge process. To better understand the difference between the investigated LVP samples and to collect information on the lithium diffusion, CV curves at scan rates ranging from 0.05 to 1.0 mV s⁻¹ were recorded. Figure 4 b shows, as an example, the variation of the CV profiles observed for the LVP/PYR₁₄TFSI electrode (the CV curves of the other electrodes can be found in Figure S4). As shown, upon increasing the scan rate the peak current increased: moreover, the

cathodic and anodic peaks moved to lower and higher potentials, respectively. This shift, which is typical for composite electrodes, is caused by polarization of the electrode at higher scan rates and is indicative of a reduction in the reversibility of the electrochemical reactions. Nevertheless, it is important to note that such a shift is not dramatic, and even the CV curve of LVP/PYR₁₄TFSI at relatively high scan rates keeps its highly symmetric shape. To quantitatively evaluate the lithium-diffusion processes of the LVP/PYR14TFSI electrodes, the peak currents (i_p) at different scan rates were plotted against the square root of the scan rate $(v^{1/2})$.^[31] (The same evaluation was performed for the other electrodes and is reported in Figure S4, in which the details concerning the calculation are also indicated.) As shown in Figure 4c, a linear relationship between i_{p} and $v^{1/2}$ was found for all samples, and this indicates a diffusion-limited intercalation process in the solid-state phase (see Table S2). Figure 4d gives a graphical comparison of the calculated Li⁺ diffusion coefficient (D) for all LVP samples. Pure LVP, which does not contain any carbon coating and which has a non-uniform morphology with strong particle aggregation, displayed the lowest lithium-diffusion coefficients among all the samples. The LVP/EMIMTFSI and LVP/C electrodes display rather similar morphology and carbon content, and also the lithium diffusion coefficients were found to be very compara-

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ble. The LVP/PYR₁₄TFSI sample displayed significantly higher lithium-diffusion coefficients than the other samples. For instance, the diffusion coefficient *D* at peak b1/b2 corresponding to the extraction/reinsertion of the second 0.5 Li was $11.3 \times 10^{-9}/9.28 \times 10^{-9}$ in LVP/PYR₁₄TFSI, $1.8 \times 10^{-9}/1.14 \times 10^{-9}$ in LVP/EMIMTFSI, $1.26 \times 10^{-9}/1.41 \times 10^{-9}$ in LVP/C, and $0.189 \times 10^{-9}/0.0162 \times 10^{-9}$ cm²s⁻¹ in pure LVP. These results indicate that the presence of nanostructures has a positive influence on the lithium-ion diffusion of LVP. Their presence shortens the diffusion paths and enlarges the contact area between the active material and the electrolyte; this leads to a significant improvement in the lithium-ion diffusion observed for the LVP/PYR₁₄TFSI sample. As shown, such an improved lithium-diffusion rate occurs during the charging process as well as the discharging process.

As mentioned above, the electronic conductivity of LVP is typically low, and therefore, the realization of an effective carbon coating is needed to overcome this limit. The solid electronic conductivity of the four LVP samples was investigated by impedance spectroscopy (Figure S6). The conductivity of pure LVP and LVP/C at room temperature was 4.8×10^{-7} and 1.02×10^{-5} S cm⁻¹, respectively. These values are consistent with other reports.^[11,12] Interestingly, the conductivity of the samples prepared by using ILs was considerably higher: $1.66 \times$ 10^{-3} and 5.50×10^{-3} S cm⁻¹ for LVP/EMIMTFSI and LVP/ PYR₁₄TFSI, respectively. The higher conductivity of these latter samples is probably related to the different conductivity of the coating of the investigated LVP. As the carbonization process of ILs (carbon precursor) occurs at higher temperature than for common carbon sources, such a process might lead to the formation of a coating with a conductivity that is higher than that of traditional precursors. Considering this finding, the use of ILs during the synthetic process appears, therefore, to have beneficial effects not only on the morphology but also on the electronic conductivity of LVP.

Given that the electrochemical performance and the conductivity of the LVP/EMIMTFSI electrode appear, overall, inferior to the electrochemical performance and the conductivity of LVP/PYR₁₄TFSI, we decided not to investigate its performance further. Instead, we decided to focus only on the comparison between the conventionally carbon-coated LVP/C and LVP/ PYR₁₄TFSI. Impedance measurements show that the two electrodes display marked differences in terms of charge-transfer resistance (Figure S5). The charge-transfer resistance of the LVP/C electrode is much higher than that of the LVP/PYR₁₄TFSI electrode. This difference confirms the importance of the nanostructured morphology and the high electronic conductivity of the LVP/PYR₁₄TFSI material and its beneficial influence on contact and charge-transfer resistance, which appears to be reduced relative to that of unstructured carbon-coated LVP.

Figure 5 compares the discharge capacities of LVP/C and LVP/PYR₁₄TFSI, as obtained during tests performed by using various discharge rates ranging from 1 to 100 C. The tests were performed in the potential window of 3.0–4.3 V vs. Li/Li⁺ and a constant charging rate of 0.1 C was applied. As shown in Figure 5 a, the LVP/PYR₁₄TFSI electrode outperformed the LVP/C electrode in terms of both capacity and capacity retention at



Figure 5. Typical cycle performance of a) the LVP/C and LVP/PYR₁₄TFSI electrodes and b) the second-cycle profiles of the LVP/PYR₁₄TFSI electrode at cut-off voltages of 3.0–4.3 V ($1C = 133 \text{ mAg}^{-1}$) at various current densities in the range from 1 to 100 C with a constant charge rate of 0.1 C. c) Cycling performance of LVP/PYR₁₄TFSI at current densities of 10, 20, and 50 C.

all investigated C-rates. At 1 C, the LVP/PYR₁₄TFSI electrode delivered a comparable capacity of approximately 120 mA h g⁻¹, whereas LVP/C delivered a capacity of 110 mA h g⁻¹. At 40 and 100 C, the LVP/PYR₁₄TFSI electrode displayed a capacity of 100 and 66 mA h g⁻¹, respectively. These values are significantly higher (more than 50%) than those observed for LVP/C, which at 100 C displayed a capacity of approximately 30 mA h g⁻¹. Taking into account the mass loading and the composition of LVP/PYR₁₄TFSI, these performance results are extremely high and are among the highest so far reported for this material.

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Figure 6. a) Cyclic voltammograms of the LVP/C and LVP/PYR₁₄TFSI electrodes at a scan rate of 0.05 mV s⁻¹ over a potential range from 3.0 to 4.8 V. b) The specific capacities of the LVP/IL electrode at cut-off voltages of 3.0-4.8 V (1C = 197 mAg⁻¹) at various current densities in the range from 1 to 50 C.

Notably, after the C-rate test LVP/PYR₁₄TFSI was again able to deliver its initial capacity at 1 C, which indicates that such a test did not harm the electrode. Figure 5b shows the voltage profiles of the LVP/PYR₁₄TFSI electrode at some of the investigated charge rates. As shown, for the charge curves at 0.1 C $(1 C = 133 \text{ mAg}^{-1})$, three plateaus at 3.58, 3.67, and 4.07 V vs. Li/Li⁺ are observed, which correspond to the extraction of lithium ions and the phase transitions of $\text{Li}_x V_2(\text{PO}_4)_3$ from x = 3.0to 2.5, 2.0 and 1.0, respectively. The first lithium ion is extracted over two steps (3.58 and 3.67 V) because of the existence of an ordered $Li_{2.5}V_2(PO_4)_3$ phase at a mixed V^{3+}/V^{4+} oxidation state. Then, single-step removal of the second lithium ion at 4.07 V can be observed, which corresponds to the complete oxidation of V^{3+} to V^{4+} . Three corresponding plateaus at 4.06, 3.66, and 3.58 V vs. Li/Li⁺ during the discharge process are attributed to the reinsertion of two lithium ions that accompany the phase transitions of $Li_xV_2(PO_4)_3$ from x = 1.0 to 2.0, 2.5, and 3.0, which is in good agreement with the CV measurements.

If higher C-rates were applied, as expected, the voltage plateaus became less defined, but even at 100 C the presence of different plateaus was still visible from the voltage profile. Notably, the LVP/PYR₁₄TFSI sample contains a limited amount of carbon (2.4 wt%), and therefore, these results have to be attributed to the enhanced electronic conductivity and ionic diffusion coefficient of the LVP obtained by the IL-assisted synthesis method.

To verify if the excellent performance of the LVP/PYR₁₄TFSI electrode could be maintained during prolonged cycling, 100 cycles at 10, 20 and 50 C were recorded. In this test, the same C-rate was applied for the charge and discharge processes. As shown in Figure 5 c, at 10 C the LVP/PYR₁₄TFSI electrode displayed a stable discharge capacity of approximately 108 mAhg⁻¹ and a decrease in the capacity to lower than 5% after 100 cycles. At 20 and 50 C, the LVP/PYR₁₄TFSI electrode still delivered discharge capacities of approximately 105 and 67 mAhg⁻¹, respectively, and it showed a remarkable cycling stability over 100 cycles. These results clearly indicate that LVP/PYR₁₄TFSI is a very promising candidate for the realization of high-performance batteries and hybrid high-power devices.

As mentioned in the Introduction, LVP can theoretically reversibly deliver 3Li⁺ ions per formula unit within a potential range from 3.0 to 4.8 V vs. Li/Li $^+$, which results in a maximum discharge capacity of 197 mAhg⁻¹. The extraction of the third lithium ion, however, is less reversible than the extraction of the first two lithium ions. Moreover, the capacity drops rapidly at such a high voltage (4.8 V) owing to electrolyte decomposition and vanadium dissolution in the electrolyte.^[31] Therefore, even if appealing, the use of LVP at 4.8 V vs. Li/Li⁺ is at present very challenging. Figure 6a compares the CV curves of LVP/ PYR₁₄TFSI and LVP/C in the voltage range from 3.0 to 4.8 V vs. Li/Li⁺. As shown, both electrodes display four oxidation peaks and three reduction peaks. The oxidation peak at 4.62 V is the extraction of the third lithium ion, associated with the phasetransition process from LiV₂(PO₄)₃ to V₂(PO₄)₃. However, the corresponding reduction peak in the CV curves is absent. In agreement with previous studies, we find that the initial reinsertion of a lithium cation into $V_2(PO_4)_3$ forms a solid solution of two phases.^[34, 35] Notably, the potential difference in the redox process for the LVP/PYR14TFSI electrode is smaller than that for LVP/C. This difference indicates that the process occurring in LVP/PYR₁₄TFSI shows a higher reversibility and a lower ohmic resistance than LVP/C. This high reversibility, which is due to the morphological characteristics of LVP/PYR14TFSI, and the effective carbon coating could be of importance in view of the use of LVP at 4.8 V vs. Li/Li⁺. Taking this point into account, we therefore performed a C-rate test in the range from 3.0 to 4.8 V vs. Li/Li⁺ (considering a nominal capacity of 197 mAhg⁻¹) by using the LVP/PYR₁₄TFSI and LVP/C electrodes. As shown in Figure 6b, LVP/PYR₁₄TFSI outperformed conventionally carbon-coated LVP/C in these tests. The capacity of the LVP/PYR₁₄TFSI electrode is higher at each investigated C-rate. Moreover, it is very important to stress the fact that although LVP/C lost capacity during every cycle, LVP/PYR₁₄TFSI displayed, after an initial small fading, constant capacity values at all investigated C-rates. It is very interesting that after the C-rate test, the LVP/PYR₁₄TFSI electrodes were able again to deliver their initial capacity at a rate of 1 C, which indicates that the test did not irreversibly harm the electrode. In contrast, the LVP/C electrodes were not able to deliver their initial capacity after the C-rate test, which is indicative of irreversible deterioration of the material. Taking these results into account, the realization of nanostructured LVP particles with a uniform and effective carbon coating appears as a promising strategy to improve the reversibility of the full delithiation of LVP.

Conclusions

In conclusion, a facile and novel procedure was reported for the use of an IL as a solvent and carbon precursor for the preparation of nanostructured carbon-coated LVP particles. The selection of a highly viscous and thermally stable IL, such as PYR₁₄TFSI, might promote the formation of nanostructures (e.g., nanorod-like) during the sol-gel synthesis. The presence of these structures shortens the diffusion paths and enlarges the contact area between the active material and the electrolyte, which leads to a significant improvement in lithium-ion diffusion. At the same time, the use of PYR₁₄TFSI has also a positive influence on the coating of the LVP particles and it improves the electronic conductivity of this material, which leads to enhanced charge-transfer properties. Cathodes containing these nanostructured LVP particles displayed excellent performance in terms of specific capacity, capacity retention (up to 100 C), and cycling stability. Moreover, the morphology and carbon coating of the investigated LVP material improved the reversibility of the full delithiation process. This simple synthesis could be easily extended to other materials. Additionally, taking into account the large number of ILs available and their different properties, a variety of different structures could be obtained depending of the selected ILs.

Experimental Section

Materials synthesis

Typically, V_2O_5 and $H_2C_2O_4$, $2H_2O$ in a stoichiometric ratio of 1:3 were dissolved in deionized water under magnetic stirring at 80 °C until a clear blue solution was formed [Eq. (1)]. To obtain the LVP/C sample, sucrose (2.5×10^{-3} mol LVP, 0.12 g) was dissolved in the solution. Then, a mixture of stoichiometric NH₄H₂PO₄ and Li₂CO₃ was added to the solution, and the batch was vigorously stirred for 10 min at 80 °C. Either PYR₁₄TFSI or EMIMTFSI was injected into the LVP precursor solution to obtain the LVP/PYR₁₄TFSI or LVP/EMIMTF-SI sample. Pure LVP was prepared without the addition of IL or sucrose. The mixed precursor was vigorously stirred at 80 °C. Thereafter, the solution was dried at 100 °C, and the dried precursor was ground and afterwards decomposed at 350 °C under an argon atmosphere for 4 h. The pre-calcined precursor was ground and treated at 800 °C for 8 h under an argon atmosphere [Eq. (2)].

$$V_2O_5 + 3H_2C_2O_4 \rightarrow 2VOC_2O_4 + 2CO_2 + 3H_2O$$
(1)

 $4 \text{ VOC}_2\text{O}_4 + 3 \text{ Li}_2\text{CO}_3 + 6 \text{ NH}_4\text{H}_2\text{PO}_4 \rightarrow 2 \text{ Li}_3\text{V}_2(\text{PO}_4)_3 + 9 \text{ CO}_2 \tag{2}$

 $+2 \text{CO} + 6 \text{NH}_3 + 9 \text{H}_2 \text{O}$

Materials characterization

The crystalline structure was characterized by X-ray diffraction (XRD) by using CuK_{a1} radiation with a Bruker D8 Advance (Germany) for 4 s at each 0.02° step width from 20 to 70°. Lattice parameters were determined by Rietveld refinement with TOPAS (Bruker) software. The morphology was characterized by a scanning electron microscope (SEM, Auriga, Carl Zeiss) with an acceleration voltage of 5 kV and ×10000 magnification and transmission electron microscopy (TEM, Zeiss LIBRA 200FE). The amount of carbon in the final product was evaluated by elementary CHN combustion analysis. Raman spectroscopy was performed by using a SENTERRA Raman spectrometer (BRUKER Optics) equipped with a 532 nm laser and an output power of 5 mW. The samples were screened with the Raman spectrometer and microscope with a 5×5 pattern in an area of 25×25 μ m, and the resulting spectra normalized and averaged.

The surface composition of the prepared LVP materials was investigated by X-ray photoelectron spectroscopy (XPS). Prior to the measurements, the materials were pressed into pellets to obtain a smooth surface with improved signal intensity. The XPS measurements were performed with an AXIS Ultra DLD (Kratos) by using monochromatic AlK_a radiation. Core scans were performed at pass energies of 20 eV. The analysis area was approximately 300×700 μ m. The calibration of the spectra was done with respect to adventitious carbon (285 eV). Quantitative analysis was performed by using the CasaXPS software. Average values were calculated from measurements at two spots.

The electronic conductivity was evaluated by impedance spectroscopy with a Novocontrol AN-alpha analyzer as an alternating current (AC) frequency generator and a POT/GAL 20/11 electrochemical test station. Approximately 20 mg of each material was pressed with a force of 150 kN cm² into pellets of 9 mm diameter and a thickness in the range from 0.14 to 0.15 mm. Each pellet was sputter coated with Au for 120 s at 45 mA from top and bottom. Impedance spectroscopy was performed in the frequency range from 100 mHz to 10 MHz at an AC voltage of 1 V.

Electrochemical measurements

For the preparation of the electrodes, 85% LVP, 10% conducting agent (Super C65, TIMCAL), and 5% binder (polyvinylidene fluoride, PVDF) were mixed in N-methyl-2-pyrrolidone and stirred overnight. The slurry was casted immediately on aluminum foil by using a laboratory-scale doctor blade coater, the blade of which was set to a wet film thickness of 200 μ m. The coated electrode was immediately predried in an atmospheric oven with stagnant air at 80 °C for 12 h. Disc electrodes with a diameter of 12 mm were cut from the so-obtained electrode tapes. The disc electrodes were dried at 120°C under vacuum for 24 h. The electrode area was 1.13 cm², and the loading density of the electrode was approximately 2.5-3.5 mg cm⁻². All the electrochemical tests were performed with three-electrode Swagelok-type cells. The cells were assembled in an argon-filled glove box with oxygen and water contents lower than 1 ppm. Metallic lithium (Chemetall) was used for both the counter and reference electrodes, a Whatman GF/D glass microfiber filter of 675 μm thickness and 13 mm diameter was used as a separator, and 1 M LiPF₆ (dissolved in ethylene carbonate and dimethyl carbonate in a 1:1 volume ratio) as the electrolyte.

All electrochemical tests were performed at room temperature [(20 ± 2) °C] with a MACCOR Battery tester 4300. All voltage quoted refer to the Li/Li⁺ couple. The galvanostatic charge and discharge

experiments within the voltage range from 3.0 to 4.3 V (1C= 133 mAg⁻¹) and from 3.0 to 4.8 V (1C= 197 mAg⁻¹) (vs. Li⁺/Li), respectively. Cyclic voltammetry (CV) was conducted at scan rates of 0.05 to 0.5 mVs⁻¹ in potential ranges from 3.0 to 4.3 V (vs. Li⁺/Li) and from 3.0 to 4.8 V (vs. Li⁺/Li). Electrochemical impedance spectroscopy (EIS) measurements were performed with a sinusoidal signal of 5 mV over a frequency range from 500 kHz to 10 mHz.

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