NASICON-Structured LiGe$_2$(PO$_4$)$_3$ with Improved Cyclability for High-Performance Lithium Batteries

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LiGe$_2$(PO$_4$)$_3$ (LGP) with a NASICON structure is synthesized through the solid state method. Well-crystallized LGP obtained at 900 °C shows a total lithium (Li) ion conductivity of 7.2 × 10$^{-7}$ S/cm. For the first time, the Li reversible capability of bulk LGP is measured to be 460 mAh/g at a charge rate of 150 mA/g in the voltage range from 0.001 to 1.5 V. Very good capacity retention of 92% after 25 cycles is achieved in comparison to 28% of GeO$_2$. At a very high charge rate of 1500 mA/g the LGP reveals excellent capacity retention of 77% after 1000 cycles. The average discharge and charge plateau is in the range from 0 to 0.4 V vs. Li. Mechanisms for the improved cycling performance of the LGP in comparison with GeO$_2$ are discussed, suggesting that Li$_3$PO$_3$ acts as a more stable and conductive inactive matrix to buffer volume expansion during Li alloying. Our results may suggest a direction to design better material systems with a combination of active and inactive materials.

1. Introduction

Lithium ion batteries (LIBs) are now intensively studied for the applications in large scale energy storage aiming at electric vehicles due to their high special energy and low pollution.$^{1-3}$ The currently common commercially used anode material for LIBs is graphite, which only has an ideal capacity of 372 mAh/g,$^{4,5}$ limiting the energy density of the battery. To increase the capacity, Li alloys including Si, Sn, Al, Sb, Pb, In, Zn, and Ge$^{6-22}$ have been considered as possible anodes for LIBs owing to their low operating voltage, high volume energy density, and high theoretical capacity.$^7$ Among which, the Ge−Li system has a high theoretical capacity of 1600 mAh/g by forming Li$_{22}$Ge$_5$, a low working potential of about 0 to 0.4 V vs. Li, and relatively high Li diffusivity at room temperature (400 times higher than well-studied Si). Ge thin films are reported to have a capacity of 500−800 mAh/g at the charge−discharge rate of 1000 C,$^{27}$ suggesting that Ge can be a promising anode for lithium ion batteries. However, like all the other Li-alloy processes,$^{20-26}$ the Ge electrode also undergoes a volume change of 370% during Li alloying and dealloying processes, leading to rapid capacity fade,$^{27-29}$ which will be worsened in the case of big the particles and the thick active film used.

To buffer the volume expansion during the alloying progress, many different mechanisms have been proposed.$^{28,30-36}$ One of these mechanisms is to decrease the volume density of electroactive elements in order to reduce the stress of volume expansion, such as forming nanometer Ge particles, nanowires, or thin films. This method shows improved cyclability.$^{30-36}$ However, the pure nanosize Ge particles can aggregate into large particles and pulverize with cycling, causing electric contact problem and hence rapid capacity loss.$^{33,35}$ To achieve good cyclability, inactive matrix buffer layers such as metal,$^{30}$ carbon,$^{31-35}$ or oxide$^{36}$ are therefore used. The matrix can hinder the aggregation of the nano Ge particles and remain electrically conductive as well. However, it is still a big challenge to get highly dispersed Ge nanoparticles embedded in the buffer matrix.$^{34}$ A alternative way is to use Ge compounds, assumed as GeX. The mechanism has been proved by the groups of Dahn$^{38}$ and Huggins$^{39}$ in the tin-based compounds where the MX will form an inactive amorphous LiX matrix and nano electroactive M particles by electrochemical reduction during the first discharge. The inactive matrix and active particles produced in this way are well dispersed in Armstrong to the nanosize level. The inactive matrix not only acts as a buffer to hinder volume expansion and aggregation of the active nanoparticles, but it also acts as a binder to keep the integrity of the active nanoparticles in contact with the current collector. Dahn$^{38}$ pointed out that the matrix is a key factor controlling the cyclability of the compounds. An ideal matrix should allow rapid transportation of the Li ion and should have a stable structure to hinder the aggregation of active nanoparticles. The most commonly used inactive matrix in the composite is Li$_2$O. During a discharge process, the following reaction takes place$^{26-29}$

$$\text{GeO}_2 + 4\text{Li}^+ \rightarrow \text{Ge} + 2\text{Li}_2\text{O} \quad (1)$$

$$\text{Ge} + x\text{Li} \leftrightarrow \text{GeLi}_x \quad (x < 4.4) \quad (2)$$

Since the GeO$_2$ anode shows poor cyclability, its capacity of discharge falls from 740 to 225 mAh/g after only ten cycles, and the fading mechanism is believed to be caused by lost contact between the active material and the current collector due to volume expansion and formation of a solid electrolyte interface (SEI) layer.$^{40}$ Cho et al.$^{41}$ also observed the poor cyclability of the GeO$_2$ glass. Through a comparison between GeO$_2$ and GeS$_2$ glass, they concluded that for LiX, the inactive matrix is the key that determines the cyclability of GeX compounds.

In this paper, a well-crystallized LiGe$_2$(PO$_4$)$_3$ (LGP) with NASICON structure has been synthesized by a solid state method. For the first time the LGP is tested as the anode for Li batteries. The LGP is known as a fast lithium ion conductor with a theory capacity of 540 mAh/g with formation of
Li$_2$Ge$_2$O$_4$. Reduction of LGP will form a Li$_3$PO$_4$ matrix surrounding electroactive Ge particles that has a stable 3D network and is a Li ion conductor with a Li ion conductivity of 8.62 $\times$ 10$^{-8}$ S/cm. The conductive matrix may provide a buffer to accommodate the volume expansion and hence to enhance the rate capability. Through the comparison of physical and electrochemical properties between LGP and GeO$_2$, it can be concluded that LGP with Li$_3$PO$_4$ matrix has an improved cyclability over that of the GeO$_2$ with Li$_2$O matrix. The results may also suggest a direction to design better composite materials for lithium batteries.

2. Experimental Section

2.1. Synthesis of LGP. LGP was synthesized through a typical solid state method. Li$_2$CO$_3$ (99%), GeO$_2$ (99%), and NH$_4$H$_2$PO$_4$ (98%) of analytical grade (all from Aldrich, USA) in a stoichiometric ratio were thoroughly mixed by ball milling for 48 h and then heated in a platinum crucible at 400 °C for 2 h to release the volatile compounds. The powder was reground and ball milled for another 24 h followed by a second calcination for 24 h at different temperatures with a heating rate of 1 deg/min.

2.2. Characterization. The structures of the as-synthesized LGP powders and those charged/discharged to different potential states were measured with a Shimadzu XRD-6000 X-ray diffraction with Cu Ka radiation ($\lambda$ = 1.5406 Å), at a scan rate of 2 deg/min. Surface morphology of the LGP power and electrodes before and after charge/discharge were characterized with a Hitachi S-4100 field emission scanning (FE-SEM) electron microscopy. For XRD and SEM examination of the electrodes after charge/discharge, the electrode films were washed with tetrahydrofuran and then dried in a vacuum at room temperature before characterization. The detailed process can be found elsewhere.

2.3. Electrochemical Measurements. Measurement of AC impedance was carried out with a Solartron impedance analyzer (model 1260) in the frequency range between 10$^{-1}$ and 10$^6$ Hz based on Wilkening et al. To study the ionic conductivity of the LGP, the LGP powder was pressed into a pellet of 1 mm thickness and 0.55 cm$^2$ area at 10 MPa, and the pellets were placed in a platinum holder and then dried at 120 °C in a vacuum for 10 h. Pt was coated on both sides of the pellet, followed by heating the Pt-coated specimen to 400 °C for half an hour. The Pt-coated pellets were assembled into a cell using stainless steel (SS) as a current collector to test the AC impedance. To test the AC impedance of the cell at different lithium intercalation states, the cell was charged or discharged to a given potential at 0.1 C (50 mA/g), and then the potential was kept for 2 h to fully reduce polarization before testing.

To evaluate the electrochemical performance of the LGP as an anode, cyclic voltammetry and battery tests were carried out with a Solartron 1287 and 1256 two-terminal cell test system with a Lab-made cell. The working electrode was made of 70% LGP or GeO$_2$, 20% acetylene black, and 10% PTFE binder on a Ni foam foil, and then was dried at 120 °C in a vacuum for 24 h. The loading material of the LGP electrode is about 3–5 mg/cm$^2$ with a thickness of about 0.1 mm. A Li foil was used as both counter and reference electrodes. LiPF$_6$ (1 M) in EC: EMC:DMC (1:1:1 in volume) solution (1/1/1 vol % Merk) was used as the electrolyte. The cell was assembled in the argon-filled glovebox with moisture and oxygen pressure below 0.1 ppm. The galvanostatic charge/discharge cycling experiment was performed in the potential range from 0.001 to 1.5 V at different C rates (assuming 1 C = 500 mA/g).

3. Results and Discussion

Figure 1 shows the XRD pattern of the LGP synthesized at different temperatures for 24 h. It can be seen that at a low synthesis temperature of 700 °C, only a slight peak of LGP can be seen, and when the temperature is increased to 800 °C, the main NASICON structure (JCPDS 41-0034) appears but with some impurity peaks. At 900 °C, a pure and well-crystallized NASICON structure (R3c) is obtained. Further increasing the temperature to 1000 °C results in an extra second phase such as GeO$_2$ (JCPDS 43-1016) and Li$_2$P$_2$O$_7$ (JCPDS 13-0282) due to Li loss at high temperature. Therefore synthesis at 900 °C is a suitable temperature for LGP.

The morphologies of the samples are shown in Figure 2. It can be seen that the morphology of the samples is highly dependent on the synthesis temperature. The samples synthesized at 700 and 800 °C are obviously not fully calcined with small particles, while the sample synthesized at 900 °C reveals a very uniform morphology with particle size about 2 µm. However, when the temperature is increased to 1000 °C, the particle size increases to about 3 µm with some heterogeneous impurities on top of the LGP particles due probably to the decomposition of LGP at high temperature.

A typical impedance plot (Nyquist plot) of LGP obtained at 298 K is shown in Figure 3. Two semicircles and a straight line are observed in the measured Li ion conductor. The straight line at low frequencies represents the Warburg impedance of the LGP associated with Li diffusion. The impedance plot could be well resolved into bulk resistance at low frequencies and grain boundary conductivities. The high Li ion conductivity may help the full reduction of LGP during the first discharge process.

Figure 4 shows the first and second cycling voltammetry curves of the LGP and GeO$_2$ based electrodes cycled at 0.1 mV/s between 0.001 and 3 V, from which it can be seen that they show almost the same profiles during the first cycle as reported by Pena et al. Both LGP and GeO$_2$ show a wide irreversible peak between 0.4 and 0.8 V (vs. Li/Li$^+$) due to the reduction of Ge$^{4+}$ to Ge accompanied by the formation of Li salt inactive matrix. Between 0 and 0.4 V, another reducive
peak appears due to the Li—Ge alloying process.\textsuperscript{35,36,40,43} When cycled to the positive direction, an oxidation peak is observed clearly corresponding to the reduction peak between 0 and 0.4 V. This pair of peaks still exist in the second cycle while the peak between 0.4 and 0.8 V has vanished. The reversible peaks between 0 and 0.4 V are due to Ge alloying and dealloying with Li. The mechanism can be concluded as follows:

\begin{equation}
\text{LiGe}_2(\text{PO}_4)_3 + 8\text{Li}^+ + 8e^- \rightarrow 2\text{Ge} + 3\text{Li}_3\text{PO}_4 \quad (3)
\end{equation}

\begin{equation}
\text{Ge} + x\text{Li}^+ + xe^- \leftrightarrow \text{GeLi}_x \quad (0 < x < 4.4) \quad (4)
\end{equation}

From Figure 4 it is clear that the CV curve of the LGP is more symmetrical and sharper than that of GeO\textsubscript{2}, implying a higher Li\textsuperscript{+} diffusion rate in the Li\textsubscript{3}PO\textsubscript{4} matrix than in Li\textsubscript{2}O.

Figure 5 shows the voltage profiles and capacity retention of both Li/GeO\textsubscript{2} and Li/LGP half cell in the first 25 cycle between 0.001 and 1.5 V at a charge/discharge current of 150 mA/g. The first discharge capacity is 2040 mAh/g for Li/GeO\textsubscript{2} half cell corresponding to 8 mol of Li\textsuperscript{+} ion adsorbed per mole of GeO\textsubscript{2}. However, the real Li absorption is less than 8 mol per mole as SEI formation will also cost Li ion. The first charge capacity is 650 mAh/g corresponding to only 2.5 mol of Li ion extracted from 1 mol of GeO\textsubscript{2}. The capacity decreases from 650 mAh/g to 180 mAh/g after 25 cycles with capacity retention of only 28%. The sharp capacity loss is mainly due to the repeated volume changes during charge and discharge in the electrode as reported before.\textsuperscript{40,41} Due to the expansion, the active material loses electronic contact with the current collector. For the LGP the first discharge capacity is 1230 mAh/g corresponding to 19.8 mol of Li absorbance. The first Li reversible capacity during dealloying is 464 mAh/g, which corresponds to 7.6 mol of Li alloying intake with formation of an average \text{Li}_3.8\text{Ge}, which is higher than that in the GeO\textsubscript{2} anode. The high reversibility is attributed to the high Li ionic conductivity of LGP compared with GeO\textsubscript{2}, since high ionic conductivity eases the complete lithiation of the bulk LGP particles during the LGP reduction.
Capacity still remains 92% after 25 cycles, showing a distinguished cycling improvement. As the only difference between LGP and GeO2 electrodes after the first discharge process is the inactive metrics of Li3PO4 and Li2O, respectively, surrounding Ge nanoparticles,41 it can therefore be concluded that the Li3PO4 matrix may provide a better buffer to accommodate volume changes during Ge alloying and dealloying with Li, the same as the Li2S matrix reported by Cho et al.41

The rate capacity of the LGP between 0.001 and 1.5 V was also measured. As shown in Figure 6, the specific current increases after 10 cycles in steps from 150 mA/g (0.3 C) to 1500 mA/g (3 C). The specific capacity decreases from 460 mAh/g to 375 mAh/g when the discharge rate increased from 0.3 C to 1.5 C (750 mA/g), and the capacity further decreases to about 240 mAh/g at a 3 C rate (1500 mA/g). The capacity increases to about 430 mAh/g when the charge rate returns to 0.3 C. At each step, the capacity remains fairly stable on cycling.

To test the stability of the LGP between 0.001 and 1.5 V was also measured. As shown in Figure 6, the specific current increases after 10 cycles in steps from 150 mA/g (0.3 C) to 1500 mA/g (3 C). The specific capacity decreases from 460 mAh/g to 375 mAh/g when the discharge rate increased from 0.3 C to 1.5 C (750 mA/g), and the capacity further decreases to about 240 mAh/g at a 3 C rate (1500 mA/g). The capacity increases to about 430 mAh/g when the charge rate returns to 0.3 C. At each step, the capacity remains fairly stable on cycling. To test the stability of the LGP, static current charge–discharge experiments are perform between 0.001 and 1.5 V at a 3 C rate for 1000 cycles. As shown in Figure 6b the capacity remained at about 77% (215 mAh/g) of the initial charge capacity after 1000 cycles. The fluctuation in capacity during cycling is believed to be caused by the buffering process of the Li–Ge alloying and dealloying process.

To study the mechanisms of the improved cyclability of the LGP, the morphologies of the LGP and GeO2 electrodes in the as-prepared state and after 25 cycles were examined, using an FE-SEM. The as-prepared GeO2 and LGP active materials are all embedded in the conducting carbon black and held together by binder (Figure 7a,b). However after 25 cycles, the GeO2 electrode changes into a loose form with many particles unconnected. This situation was also observed by Pena et al.36,38 In contrast to the GeO2 electrode, the LGP electrode retains its uniformity and integrity after 25 cycles. The tidy connection structure reduces capacity lose. Since the difference between GeO2 and LGP is only the different matrix, it can therefore be concluded that the Li3PO4 matrix formed in LGP is more stable than the Li2O matrix formed in GeO2.

Ex situ XRD measurements of the LGP were performed to investigate the Li+ reaction mechanisms in LGP. For a comparison, as-synthesized LGP is given in Figure 8a. As shown in Figure 8b, when the cell is discharged to 0.4 V in the first cycle, the intensity of the diffraction peaks of LGP is greatly reduced, and broad peaks between 22° and 24° correspond to Li3PO4 (22.20° JCPDS 45-0747) and GeLi\textsubscript{x} (23.46° (Li\textsubscript{7}Ge\textsubscript{2}), JCPDS 29-0636, 22.24° (Li\textsubscript{11}Ge\textsubscript{6}) JCPDS 29-0803, 23.1° (Li\textsubscript{15}Ge\textsubscript{4}) JCPDS 89-2584), indicating different lithiation phases during the alloying process. The broad peaks instead of sharp peaks are a well-known duo to the nanoscale or amorphous state of the reduction products. The same phenomenon is also observed by Cho.41 An almost invisible little broad hump at 2θ = 32.8° indicates the existence of Ge (JCPDS 18-0594). When the cell is discharged to 0.001 V, all the LGP peaks completely vanish, instead there is the formation of an amorphous-like hump between 21° and 24° due to the Li3PO4 and Ge–Li alloys, and a very weak peak at about 34° (Ge\textsubscript{5}Li\textsubscript{22} JCPDS 17-0402) due to the final amorphous phase mixture of Li3PO4 and GeLi\textsubscript{x} (Figure 8c).40 The electrode remains in the amorphous state after 25 cycles, suggesting there is no crystallization of Ge and Li3PO4 during cycling (Figure 8d). The same XRD patterns were also

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**Figure 5.** Comparison of the first 25th galvanostatic cycles of LGP/Li (a) and GeO2/Li (b) half cell at 150 mA/g with a cutoff voltage between 0.001 and 1.5 V.

**Figure 6.** Rate capabilities of the LGP at a cutoff voltage from 0.001 to 3 V: (a) respectively cycled at 150, 750, and 1500 mA/g and (b) after 1000 charge/discharge cycles at the rate of 1500 mA/g.
observed by Pena\textsuperscript{40} and Cho\textsuperscript{41} in GeO\textsubscript{2} and GeS\textsubscript{2}, and by Dahn\textsuperscript{38} in SnO\textsubscript{2}. They ascribed the wide XRD peaks to the small GeLi\textsubscript{x} domain and the amorphous lithium salt matrix.\textsuperscript{36,38,40} The mechanism of LGP to react with Li\textsuperscript{+} can be concluded as

$$\text{LiGe}_2(\text{PO}_4)_3 + 8\text{Li}^+ - 8e \rightarrow 2\text{Ge} + 3\text{Li}_3\text{PO}_4$$ (5)

$$\text{Ge} + x\text{Li}^+ - xe \rightarrow \text{GeLi}_x \quad (0 < x < 4.4)$$ (6)

Since nanosized Ge particles are embedded in the matrix of amorphous Li\textsubscript{3}PO\textsubscript{4}, the matrix buffers the volume expansion and hence hinders the aggregation of Ge during the Ge–Li alloying and dealloying process.

Electrochemical impedance spectroscopy (EIS) studies were carried out by using the LGP/Li half cell to study the kinetic mechanisms of Li transportation. In the EIS study, the LGP composite electrode was used as a working electrode and a Li foil as an anode and a reference electrode. The cells were charged or discharged to a given potential at 0.1 C (50 mAh/g) and then balanced at the potential for 2 h before the impedance data were collected. The results are typically Nyquist plots. The electrochemical impedance spectroscopy at the open circuit potential (OCP) shows a semicircle at high frequency and a straight line at low frequency as shown in Figure 9. This is a typical Li ion blocking process. The left intercept at the Z' axis in high frequency corresponded to the resistance of the electrolytes. The semicircle is well-known to be attributed to the surface film impedance of the lithium counter electrode (coupled with interfacial and/or surface films capacitances), and the straight line at the low-frequency part is due to the bulk transport processes (Li ion diffusion in LGP bulk).\textsuperscript{48-50} When the cell are discharged to 0.4 V, the total resistance increased about 30% due clearly to the new resistance of the surface electrode interface (SEI) film produced on the LGP electrode by the solvent reduction products beginning at 0.8 V, as at this potential, no other charge transfer process of LGP has occurred.\textsuperscript{39-41} When the cell is discharged to 0.001 V, the resistance is further increased due to the thickening of the SEI film on the LGP electrode. Meanwhile, a new semicircle
appeared in the middle frequency due to the charge transfer resistance during the reduction of the LGP and lithium alloying with freshly formed germanium.\(^9\) In the corresponding first charging process, when the cell is charged to 1.5 V, the middle frequency due to charge transfer is greatly decreased and only the high-frequency semicircle due to the SEI film resistance appears. The change is caused by the full delithiation of the Ge—Li alloy at high voltage. As indicated above, no charge transfer due to the Li—Ge alloying has occurred in this potential range.\(^9\) Similar EIS graphs are found in Sn, Si-containing compounds.\(^49-53\) The EIS data after 25th cycles show almost the same tendency as the first cycle with only little changes in both the SEI film resistance and charge transfer resistance value. These results further improved the theory that the germanium incorporated in the Li\(_3\)PO\(_4\) matrix is electrochemically stable and reversible during the Li—Ge alloying and dealloying.

4. Conclusions

NASICON-structured LiGe\(_2\)(PO\(_4\))\(_3\) (LGP) is successfully synthesized through a solid state reaction at 900 °C for 24 h. Well-crystallized NASICON particles of about 2 μm are obtained. The LGP shows a total Li ion conductivity of 7.2 × 10\(^{-7}\) S·cm\(^{-1}\). In galvanostatic cycling, the LGP shows a low working plateau between 0.001 and 0.4 V vs. Li and possesses a reversible capacity of 460 mAh/g at a charge/discharge rate of 150 mA/g through alloying and dealloying mechanisms. The LGP also reveals good capacity retention of 92% compared to 28% of GeO\(_2\) after 25 cycles. At a high charge/discharge rate of 1500 mA/g the LGP shows 77% capacity retention after the 1000th cycle. The improved Li-cycling performance of the LGP is associated with formation of the Li\(_2\)PO\(_4\) matrix, which can better buffer the volume expansion and hence can hinder the aggregation of small active particles. The results suggest that Li\(_3\)PO\(_4\) should be a more stable conductive matrix than Li\(_2\)O for buffering the volume expansion during the Li-alloy process. The capacity of LGP may not be very high compared to that of many materials, but long time cycle-ability material is an essential factor for commercial use; our results also suggest a direction to design better material for lithium batteries.

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References and Notes


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