All-Solid-State Supercapacitors Based on a Carbon-Filled Porous/Dense/Porous Layered Ceramic Electrolyte

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Solid-state storage devices based on ceramic electrolytes have great potential because of their high security, long cycle life, and wide working temperature. In the present work, the three-dimensional structure of a carbon-filled porous/dense/porous layered ceramic electrolyte is designed for a solid-state supercapacitor. A single phase of Li1.3Al0.3Ti1.7P3O12 (LATP) is obtained by a one-step solid-state reaction using ammonium polyphosphate (APP) as a PO4 precursor. The densification of the LATP ceramic is improved by introducing sintering aids of LiMnPO4 (LMP). Porous/dense/porous layered ceramics were then fabricated by sintering the LATP/LATP-2%LMP/LATP pellet at 825 ◦C. Carbon-filled layered ceramics show a large capacitance of 0.13 F cm−1 at a low scan rate of 2 mV s−1. The large capacitance for carbon-filled layered ceramics is due to the enhanced contact area between the electrode and solid electrolyte in the porous structure. The present supercapacitor also shows good cycling stability (∼91% of the initial capacitance after 600 cycles at a scan rate of 5 mV s−1).

Currently, energy storage devices such as commercial lithium ion batteries and supercapacitors mostly use liquid electrolytes. However, several drawbacks exist with liquid electrolytes, such as expensive sealing agents and inherent hazards of fire and leakages. To improve the safety of lithium ion batteries, nonliquid electrolyte systems such as gel-polymer electrolytes and dry polymer electrolytes have been studied.1−4 However, these systems still contain a small amount of liquid electrolyte to maintain their high ionic conductivity. All-solid inorganic batteries have been given attention because of their high reliabilities, potential durability against high temperature, and safety.5−8

Up to now, there are very limited reports on all-solid inorganic supercapacitors.9 In general, supercapacitors can be divided into two categories according to their energy storage mechanism: one type is the electrochemical double-layer capacitor (EDLC), and the other is the pseudocapacitor.10 Unlike traditional dielectric capacitors, the electrostatic charge accumulation occurs at the electrode/electrolyte interface for EDLCs. Typical materials based on an electrical double-layer mechanism have a limited specific capacitance, typically in the range of 10–50 μF cm−2 for a real electrode surface.11 However, recent experiments have reported much larger values of the EDL capacitance in phosphosilicate glasses placed between platinum electrodes.12,14−16 Current theories of EDL capacitors, based on the mean-field approach, fail to explain such a large capacitance. Shklovskii et al.12 proposed an alternate non-mean-field theory of the ionic double layer to explain such large capacitance values.

According to experimental results reported by Shklovskii et al.,12,13 the formation of ion accumulation/depletion layers between solid electrolytes and metallic or semiconductor electrodes can be used to store charge for supercapacitors. However, for commercial applications, it is essential to choose the right electrode and electrolyte materials for solid-state supercapacitors. In 2016, Kato et al.15 reported the highest lithium ionic conductivity of 25 mS cm−1 at a low scan rate of 2 mV s−1. The high ionic conductivity is found in sulfide systems, oxide systems are still attractive due to their ease of preparation and stability in air.16 One of the important types of inorganic solid-state electrolytes is the NASICON-type electrolyte, having the general formula Li1.3Al0.3Ti1.7P3O12 (LATP).17,18

In general, when using solid ceramic electrolytes, a high resistance is produced, owing to insufficient contact at the interface between the solid electrolyte and standard electrode sheet.3 Therefore, it is required to increase the contact area between the electrode and solid electrolyte in order to decrease the electrochemical interfacial resistance and increase the energy density. One promising approach is to design and integrate the electrode materials and electrolyte in a 3D configuration.19,20 In the present manuscript, a three-dimensional structure of an electrode filled with porous/dense/porous layered ceramic is designed to obtain an all-solid supercapacitor with improved electrochemical properties.

Experimental

The Li1.3Al0.3Ti1.7P3O12 and LiMnPO4 powder compositions were synthesized by a conventional solid-state reaction method using high-purity MnCO3, Li2CO3, TiO2, Al2O3, and ammonium polyphosphate (degree of polymerization 1000). The starting materials were mixed for 1 h in a ball mill with zirconia balls according to the desired stoichiometry. For Li1.3Al0.3Ti1.7P3O12 phase, the mixtures were dried and fired in an alumina crucible to check the reaction between the raw materials in the range of 400–800 ◦C for 3 h in air. The calcined powders of Li1.3Al0.3Ti1.7P3O12 and LiMnPO4 were mixed again with zirconia balls. The dried powders, with 6 wt% PVA (polyvinyl alcohol) added, were pressed into pellets under a pressure of 20,000 psi, and these compacts were sintered at temperatures from 800 to 1050 ◦C in air for 3 h. Phase constitutions were identified by X-ray diffraction (XRD) patterns using CuKα radiation (Rigaku D/max-IIIJA, Bruker).

The density of the pellets was determined via Archimedes’ method.21 There were three measurements that needed to be taken: the dry weight (W1), weight of the ceramic body in water (W2), and weight of the water-saturated ceramic body (W3). Bulk density was calculated by W3/(W3-W2). Apparent porosity was calculated by (W3-W1)/(W3-W2). To study the mechanical behavior, Vickers microhardness measurements under 9.8 N were performed (Wolpert Tukon 2100B, Wilson). SEM analyses of the indented surfaces were also carried out (EV018, Zeiss). The polyimide (PI-B) solution was dipped into porous ceramic and then treated under vacuum, followed by solidification at 210 ◦C for half an hour. Then, the PI-filled porous ceramic was carbonized in vacuum at 825 ◦C for 2 h, at a rate of 2 ◦C min−1.22 The pore structures before and after carbon coating were investigated using mercury intrusion porosimetry (Auto Pore 9500 IV, Micromeritics Instrument (Shanghai) Ltd).

For the AC impedance measurement, an Au electrode was fabricated by RF magnetron sputtering on both sides of the ceramics (JGP560 ultra-high vacuum multi-function sputtering instrument). Cyclic voltammetry and galvanostatic charge-discharge cycling were performed from 0 to 0.8 V, and electrochemical impedance spectroscopy was conducted from 0.1 Hz to 1 MHz (SP-150, Bio-Logic). The areal capacitance (AC) was calculated by dividing the charge (Q), by the area of the electrode (A) and the width of the potential window (∆V). The charge is calculated using half of the integrated area of the
cyclic voltammetry curve or by integrating the discharge current over time.

**Discussion and Results**

LATP is usually synthesized using solid-state reactions, sol-gel, hydrothermal synthesis, coprecipitation, etc. Among those techniques, the solid-state reaction method is a more developed technology and used more frequently since it is a simple synthesis method and is easy to scale up for mass production. When using a traditional PO4 precursor such as NH4H2PO4 as a raw material, the fired product is easy to agglomerate and difficult to be crushed. To simplify the synthesis process, ammonium polyphosphate (APP) is adopted as the new PO4 precursor.

XRD patterns of the product with various synthesis temperatures are shown in Fig. 1. The XRD results suggested that the following reactions may occur during calcining:

\[
\text{Li}_2\text{CO}_3 + \frac{2n}{3} (\text{NH}_4)_{3n}\text{P}_n\text{O}_{3n+1} - 2\text{LiPO}_3 + 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad [1]
\]

\[
\text{TiO}_2 + \frac{2}{3} (\text{NH}_4)_{3n+2}\text{P}_n\text{O}_{3n+1} - \text{TiP}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O} \quad [2]
\]

\[
1.3\text{LiPO}_3 + 0.15\text{Li}_2\text{O} + 0.85\text{TiP}_2\text{O}_7 + 0.85\text{TiO}_2 - \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{P}_3\text{O}_{12} \quad [3]
\]

Occurrence of any specific reaction among (1) to (3) and the final phase constitution are largely dependent on the calcination temperature. At 400 °C, Li2CO3 reacted with the APP, and the Li2PO3 (JCPDS no. 29-0793) phase formed (Eq. 1). The XRD pattern confirmed the formation of the TiP2O7 (JCPDS no. 33-0803) phase at 500 °C (Eq. 2), and the amount formed increased at 600 °C. At 700 °C, though the dominant phase was LATP, some TiP2O7 and AlPO4 (JCPDS no. 11-0500) phases were also found, and the suggested reaction is shown in Eq. 3. At 800 °C, all the peaks in Fig. 1e were attributed to the NASICON phase, and the well-crystallized phase of LATP was obtained.

Usually, the heating treatment for LATP ceramic should be limited in temperature (below 1100 °C) to limit lithium sublimation and subsequent decrease in the ionic conductivity. As shown in Fig. 2, it is difficult to obtain dense LATP ceramic without a sintering aid, even when local melting is observed at the sintering temperature of 1050 °C.

In a previous work,23 it was shown that dense LiMnPO4 ceramic could be obtained by sintering at 750 °C. Then, LiMnPO4 is introduced into LATP ceramic as a sintering aid to improve the densification process.

To check the impurity phase, compatibility tests between the ceramic oxide compounds and the sintering aid were performed. Only the characteristic peaks of LATP were observed for LATP ceramic with 2% LMP in the XRD patterns of Fig. 3, and that may be attributed to the amount of the second phase present being lower than the detecting limit of the instrument. When increasing the LMP amount to 10%, the LMP phase is observed, as shown in Fig. 3, and the coexistence of two phases is confirmed.

The densities with the sintering temperature of LATP ceramic with the sintering aid are shown in Fig. 2. The bulk densities of the sintered ceramics were measured using Archimedes’ method. With the increased content of LMP, the sintering temperature for the maximum density decreased. The maximum density was obtained for the LATP ceramic with 2% LMP (weight percent) at a sintering temperature of 825 °C, and the relative density was more than 98% of the theoretical density. The theoretical density (~2.94 g cm\(^{-3}\)) used here was calculated from the stoichiometric formula of LATP and unit cell volume (1301.15 Å\(^3\)) from the XRD pattern (Fig. 1e). The wide sintering window for LATP with 2% LMP is also favorable for mass production. The results show significant improvement by introducing the sintering aid.

**Figure 1.** XRD patterns of the mixtures according to LATP at various synthesis temperatures: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; e) 800 °C.

**Figure 2.** Densities of LATP ceramic with different amounts of LMP at various sintering temperatures.

**Figure 3.** XRD patterns of LATP with different amounts of LMP sintered at 825 °C.
From the viewpoint of practical applications, the solid electrolyte pellet should have satisfactory mechanical properties. Vickers microhardness measurements under loads of 9.8 N were performed on the most dense LATP ceramic with different amounts of sintering aids, and the measurement on the pure LATP ceramic failed due to its poor mechanical properties. The results from the Vickers hardness measurements are shown in Fig. 4a along with the density, demonstrating that there is a direct relationship between hardness and the density of ceramics. The Vickers hardness measured for LATP with 0.5% LMP was 386 HV. There was a 23% increase in hardness to 473 HV for LATP with 2% LMP. SEM analyses on the indented surfaces are shown in Figs. 4b and 4c. With the sintering aid, the mechanical properties for the ceramic have been obviously improved.

Electrochemical measurements were carried out on the LATP ceramic with 2% LMP sintered at 825°C. As shown in Fig. 5a, the Nyquist impedance plot is composed of a straight line at low frequencies (0.1 to 3382 Hz), and a depressed semicircle at high frequencies (5444 to 1 M Hz). The intercept of the semicircle in the high frequency represents the bulk resistance $R_b$, and the diameter of the semicircle is attributed to the grain boundary resistance $R_g$. The results were analyzed using an equivalent circuit model shown in the inset of Fig. 5a. The bulk electrical properties are represented by a simple series combination of the bulk resistance ($R_b$) and the grain boundary resistance ($R_g$), with a constant-phase element $CPE_g$. The impedance of the constant-phase element (CPE) is given by $Z_{CPE} = \frac{1}{Q(\omega)^{n}}$ with $n \leq 1$. The electrode/electrolyte interface is described by a parallel combination of an interfacial resistance $R_{int}$ and a constant-phase element $CPE_{int}$. The $CPE_{int}$ accounts for the nonideal capacitive behavior of the interface, which is often attributed to the distribution of double-layer capacitances caused by the roughness of the interface.

As shown in Figs. 5a and 5b, a good agreement between calculated lines with the experimental data indicates that the suggested equivalent circuit describes the pellet electrode interface reasonably well. The fitted values of different parameters are listed below:

- $R_b = 28.1$ $\Omega$ cm$^2$
- $R_g = 195.7$ $\Omega$ cm$^2$
- $Z_{CPE_g} = 3.77 \times 10^{-7}(\omega)^{-0.68}$
- $R_{int}$
- $CPE_{int}$

Figure 4. (a) Vickers hardness and densities for LATP ceramics with different amounts of LMP, scanning electron micrographs of Vickers hardness indentation marks in sintered pellets: (b) LATP-0.5%LMP and (c) LATP-2%LMP.

Figure 5. Electrochemical behaviors of LATP-2%LMP ceramic sintered at 825°C with sputtered Au electrodes: (a) impedance profile (inset: equivalent circuit); (b) frequency-dependent real part of the capacitance; (c) CV curves and (d) areal capacitance at different scan rates. (Thickness of the LATP plate: 1.09 mm).
capacitor thickness corresponding to mean field theories. However, the interface reported here could be explained by the smaller effective surface. The larger capacitance formed at the carbon/ionic conductor layer mechanism for an aqueous electrolyte have limited specific capacitance calculated from the CV curves decreased with an increase in frequency, and the bulk capacitance was reflected at high frequencies above 10 kHz. With decreasing frequency, $C'$ increased strongly, and below 10 Hz, there was a levelling-off into a tilted plateau regime reflecting the interfacial capacitance. At low frequencies, the mobile ions can follow the applied oscillating field and file up at the electrode-ceramic interface, which results in a large interfacial capacitance. On the other hand, at high frequencies, the ions cannot follow the rapidly varying electric field, and hence, the capacitance decreases and becomes constant at very high frequencies.

Fig. 5c shows the electrochemical characteristics of the ceramic with double symmetrical Au electrodes. The CV shapes show the good charge storage characteristics. The voltage window of 0.8 V is analogous to that of aqueous electrolyte and much lower than that of organic electrolytes. As shown in Fig. 5d, the areal capacitance (AC) value calculated from the CV curves decreased with an increase in the scan rate. The calculated AC value was found to be 52, 41, and 29 $\mu$F cm$^{-2}$ at scan rates of 2, 10, and 100 mV s$^{-1}$, respectively. The areal capacitance was much smaller than that for phosphosilicate glass reported by Loth et al., which was explained by non-mean field theory. As is well known, materials based on an electrical double layer mechanism for an aqueous electrolyte have limited specific capacitance, typically in the range of 10–50 $\mu$F cm$^{-2}$ for a real electrode surface. The larger capacitance formed at the carbon/ionic conductor interface reported here could be explained by the smaller effective capacitor thickness corresponding to mean field theories. However, more theoretical work still needs to be done on the double layer at electrode/solid electrolyte interfaces.

For both double layer supercapacitors and electrochemical supercapacitors, the most important parameter to affect the capacitance is the available contact area between the active electrode material and electrolyte. An effective way to increase the solid-solid contact area is to obtain a 3D interconnected structure for supercapacitors. At the same time, the close contact between electrode and electrolyte should also be achieved to ensure an effective charge transfer reaction.

To increase the contact area, carbon-filled porous/dense/porous layered ceramics were designed. Two layers of pure LATP and one intermediate layer of LATP with 2% LMP were pressed to pellets with controlled mass. The pellets were sintered at 825 °C, and porous/dense/porous layered ceramics were obtained as shown in Fig. 6a. The introduction of the dense layer could improve the ion charge transfer and prevent the electronic short circuit between two sides of electrode. As shown in Fig. 6b, the polyimide (PI-B) solution was dipped into the porous layer following solidification at 210 °C for half an hour, and then, the ceramic with PI was treated in vacuum at 825 °C for 2 h at a rate of 2 °C min$^{-1}$. As shown in Fig. 6c, the carbon-filled layered ceramic was obtained for the supercapacitor application. The supercapacitor fabricated for the present investigation consisted of 0.5 mm thick porous electrode layers and a 1 mm thick dense electrolyte layer. The optical image of layered ceramic is shown in Fig. 6d and the obvious boundaries between dense layer and carbon filled layer are found. The microstructures of the layered ceramic are also shown in Figs. 6e–6g. Compared to Fig. 6e for the dense layer, obvious interconnected pores are observed in Fig. 6f. The grain boundary or pore is clearly noticeable in Fig. 6f, while in Fig. 6g, the boundary or pores between grains are smoothed by the carbon coating. The carbon coating was continuous and filled the pores in the ceramic. Furthermore, no degradation of LATP phase heating under vacuum is found by the analysis of the XRD pattern (not given here).

The pore structures before and after carbon coating were also investigated using mercury intrusion porosimetry, as shown in Table I. A high specific surface area was obtained for porous ceramic with nanosized pores. After carbon coating, the average pore size of porous ceramic decreased. Though decreased porosity and pore size
revealed the effective carbon coating, carbon filling rate still need to be improved in future work.

The electrochemical properties of the carbon-filled layered ceramic are shown in Fig. 7. The Nyquist impedance plot shown in Fig. 7a was analyzed using the same equivalent circuit model as that for the dense ceramic shown in the inset of Fig. 5a. The fitted values of different parameters are listed below: \( R_b = 16.9 \, \Omega \, \text{cm}^2; \) \( R_g = 89.3 \, \Omega \, \text{cm}^2; \) \( Z_{\text{CPE}g} = 1.73 \times 10^{-7}(j\omega)^{-0.59}; \) and \( R_{\text{int}} = 189.1 \, \Omega \, \text{cm}^2; \) \( Z_{\text{CPE}int} = 0.021 \times (j\omega)^{-0.52}. \) The total electrical conductivity of \( 9.4 \times 10^{-4} \, \text{S cm}^{-1} \) was calculated by dividing the impedance value by the dense layer thickness (1 mm). Compared to that of the dense LATP ceramic, the increased electrical conductivity was due to the increased interface area between the porous electrode layer and dense electrolyte layer.

As shown in Fig. 7b, the dependence of capacitance on frequency could also be analyzed by the fitted equivalent circuit model. The \( n \) value of 0.52 (close to 0.5) represented the case of semi-infinite linear diffusion. When the charge carrier of Li ion diffuses through solid electrolyte, it cannot fully penetrate the layer, even at low frequencies. Compared to the \( n \) value of dense LATP ceramic as shown in Fig. 5, the lower \( n \) value for the layered ceramic is due to the lower diffusion speed of Li ion in porous structure.

As shown in Fig. 7c, the shapes of CV curves show a remarkable scan rate dependence. At a high scan rate of 100 mV s\(^{-1}\), the slope

| Table I. Microstructural properties of the sintered ceramics determined by mercury intrusion porosimetry. |
|---------------------------------------------------------------|
| Porous ceramic before carbon coating | Porous ceramic after carbon coating |
| Total intrusion volume (cm\(^3\)/g) | 0.234 | 0.189 |
| Total pore area (m\(^2\)/g) | 3.03 | 3.17 |
| Average pore radius (nm) | 155 | 119 |
| Bulk density (g/cm\(^3\)) | 1.86 | 1.87 |
| Porosity (%) | 43.5 | 35.4 |

Figure 7. Electrochemical behaviors of carbon-filled porous/dense/porous layered ceramic: (a) impedance profile (inset: equivalent circuit); (b) frequency-dependent real part of the capacitance; (c) CV curves and (d) areal capacitance at different scan rates (inset: capacitance retention at scan rate of 5 mV s\(^{-1}\)); (e) charge/discharge curves and (f) areal capacitance at different current densities.
and a narrow curve was observed, and the areal capacitance was 3.3 mF cm\(^{-2}\), as shown in Fig. 7d. However, it is important to note that the large capacitance of 0.13 F cm\(^{-2}\) was obtained at a low scan rate of 2 mV s\(^{-1}\). The capacitance of the layered ceramic before PI impregnation and carbonization was 43 μF cm\(^{-2}\) at scan rate of 2 mV s\(^{-1}\). The areal capacitance of 85 mF cm\(^{-2}\) at a scan rate of 5 mV s\(^{-1}\) was much higher than that in an all-solid-state supercapacitor based on a Li\(_2\)S-P\(_2\)S\(_5\) glass ceramic (8.7 mF cm\(^{-2}\) considering the area of 1.33 cm\(^2\)) or LATP-carbon nanotube (CNT) mixture (1.16 mF cm\(^{-2}\) considering the thickness of 1 mm).\(^{10}\) Higher areal capacitance for carbon-filled layered ceramics could be due to the enhanced contact area between the electrode and solid electrolyte in the porous structure. As shown in the inset of Fig. 7d, the present supercapacitor also shows good cycling stability (~91% of the initial capacitance after 600 cycles at a scan rate of 5 mV s\(^{-1}\)). Compared to that in the dense LATP ceramic (Fig. 5d), the huge increase in capacitance for the layered ceramics was due to the increasing contact area between the electrode and solid electrolyte in the porous structure, as shown in Fig. 6f. The area capacitance could also be improved by increasing the thickness of the pore layer or the specific surface area of the open pores.

As shown in Figs. 7e and 7d, the electrochemical behaviors in terms of the charge-discharge current were also investigated for the capacitance calculated from the discharge curves depending on the scan rate of 5 mV s\(^{-1}\). A calculated equivalent series resistance (ESR) of 134.5 Ω was obtained from equation:\(^{28}\)

\[
\text{ESR} = \frac{\text{IRdrop}}{2\text{discharge}}. 
\]

As reported by Stoldt et al.,\(^*\) increased ESR and nonideal capacitor performance can be interpreted as inhomogeneities in the nanostructured electrodes created by a poor distribution of electrode material. In present layered ceramic supercapacitors, the poor rate capability and increased ESR could be contributed by a disconnectivity of electrode material, loose contact between electrode and solid electrolyte, and unreasonable pore geometry. Furthermore, increasing filling rate of carbon could improve the capacitance characteristics.

Conclusions

In the present work, a single phase of LATP was synthesized by a one-step solid-state reaction using ammonium polyphosphate (APP) as a PO\(_4\) precursor. Dense LATP ceramic is obtainable at a sintering temperature of 825°C by incorporating 2% of the sintering aid LMP. Porous/dense/porous layered ceramics were fabricated by sintering the LATP/LATP-2%LMP/LATP pellet at 825°C. The LATP ceramic shows a typical double-layer capacitor behavior. The impedance spectra are well fitted with the equivalent circuit, which consists of a series combination of the bulk resistance (R\(_b\)), the grain boundary resistance (R\(_{gb}\)) with a constant-phase element CPE\(_gb\), and an interfacial resistance R\(_{aw}\) with a constant-phase element CPE\(_aw\). Carbon-filled layered ceramics show a large area capacitance of 0.13 F cm\(^{-2}\) at a low scan rate of 2 mV s\(^{-1}\). The large increase in capacitance for layered ceramics is due to the increased contact area between the electrode and solid electrolyte in the porous structure. The supercapacitor also shows good cycling stability (~91% of the initial capacitance after 600 cycles at a scan rate of 5 mV s\(^{-1}\)).

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