ELECTRICAL AND MECHANICAL PROPERTIES OF LiALTi(PO_4)$_3$ SOLID ELECTROLYTE-BASED POWER COMPOSITE

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Abstract

This paper introduces a new method of producing power composites which can store (and delivering) electrical energy whilst learning mechanical loads simultaneously. The composite system in the present work based on all-solid state supercapacitors by using $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ solid electrolyte which has been synthesized by sol-gel method. The as-prepared samples are embedded into fiber composite materials injected by the high-performance resin RTM-6 using Differential Pressure-Resin Transfer Moulding (DP-RTM). The mechanical properties of composite materials with and without solid electrolytes are characterized by four points bending test. The influence of loads on electrical properties is also investigated by coupling tests which combine the electrical measurements with stepwise bending loads. The results reveal that solid electrolyte embedding results in slightly decreases of bending strength and ductility. However the Young's Modulus increases dramatically. Besides, the bending loads have no obviously influence on capacitance but reduce the conductivity of solid electrolyte which can be attributed to the cracks during bending tests.

1. Introduction

Power composites showing the ability to store or generate energy have recently been developed and have attracted a great deal of attention, because of the upcoming demands for lightweight, green and safe productions in transportation modes. One type of these multifunctional composites is a structural supercapacitor which combines the function as supercapacitor and can bear mechanical load simultaneously. Supercapacitors are also called double layer capacitors, which possess high capacity, high power efficiency and long cycle life. Usually they consist of two electrodes with high surface area, a separator avoiding short-cutting between two electrodes and electrolyte providing the needed migrated ions to build up 'double layer'. In case of leakage after crash, all solid state should be realized, especially solid electrolytes [1, 2].

In our previous research [3], we already reported about an all-solid-state structural supercapacitor based on NASICON-type $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ ceramic electrolyte. The electrolyte was embedded in laminates made of fleece and metalized fleeces used as collectors. Especially the electrical properties were focused on. In this paper the corresponding mechanical characterization is in focus using four point bounding tests.

2. Experimental

2.1. Synthesize process of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ solid electrolyte

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The $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) solid electrolyte was synthesized by a sol-gel method with citric acid . Stoichiometric amounts of 0.8 mol/L Titanium (IV) t-butoxide (≥99.9%, Alfa Aesar) were dissolved in 0.2 mol/L citric acid (>99%, Merck KGaA), heated and stirred at 95°C for 20h. Then stoichiometric amounts of $LiNO_3$ (>99%, ReagentPlus®), $NH_4H_2PO_4$ (>98.5%, ReagentPlus®) and $Al(NO_3)_3{\cdot}9H_2O$ (99.2%, VWR chemicals) were added, dissolved and stirred at the same temperature for 30 min until a homogeneous solution was obtained. After that, ethylene glycol (≥99.9%, Merck Schuchardt OHG) with a molar ration of citric acid at 1:1 was added. Then the solution was heated up to 120°C with stirring for 30 min and heated up to 170°C for 2h to evaporate the water and obtain the polymer precursor. The dried gel was milled by hand into powders and transferred to a ceramic crucible, heated up to 600°C for 5 h with 5 °C/min to complete pyrolysis process and calcined in open air at 800°C for 5h. The acquired powder was milled by mechanical milling method with ethanol for 2 h and pressed into pellets (thickness 1 mm) under the pressure of 180MPa. The pellets were sintered at 950°C for 8h (heating rate is 2°C/min).

2.2 Manufacture of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ solid electrolyte-based multifunctional power composites

The solid electrolyte pellets were polished and sputtered with gold in thickness about 90 nm. Polyester fiber layers (Type Viledon T 1702, Fa. Freundenberg) were used as insulation materials and metalized polyester layers were used as electronic conductive materials.

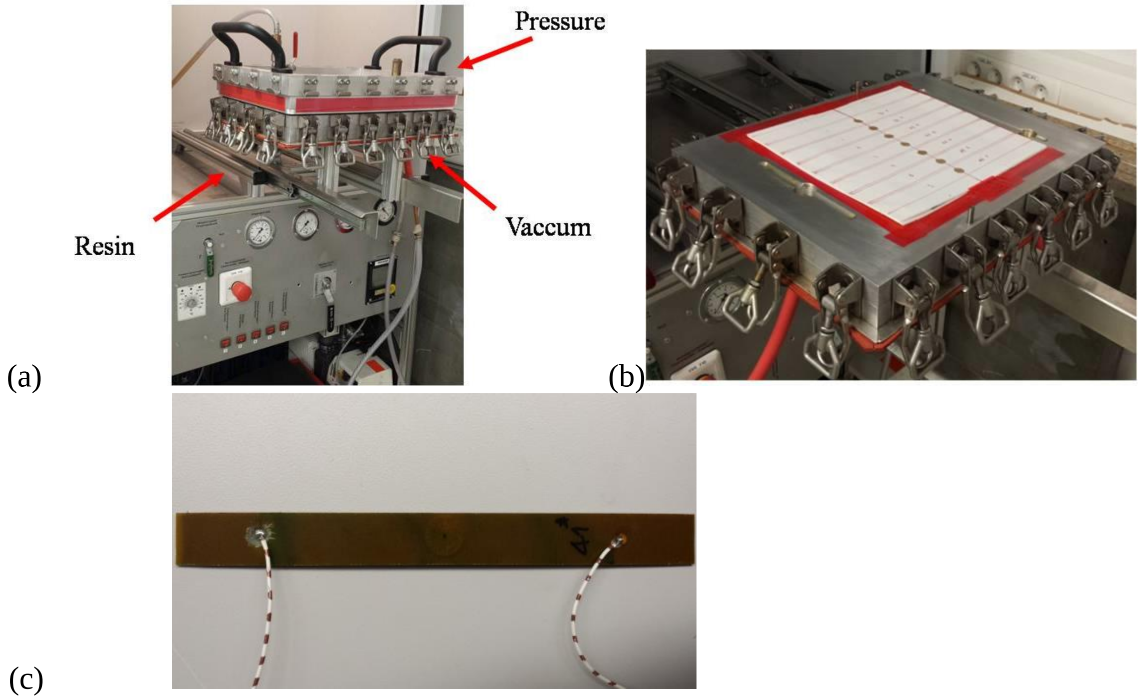

Figure 1. (a) DP-RTM system for injection process; (b) LATP embedded into fleece laminate; (c) four point bending test sample with bond points for electrical measurements

The embedding structure is shown in Fig. 1. The composite samples are produced by a process called Differential Pressure Resin Transfer Moulding (DP-RTM) [14] with injection of RTM-6 (Hexcel Composites). After curing, the plate was cut into samples for mechanical tests: samples for 4-point-bending tests are of 100×15×2 mm (according to standard DIN EN ISO 14125:1988, class IV); samples for tensile tests are of 250×25×2 mm (according to standard DIN EN 527-4) and four cap strips with width of 50mm are pasted on the both ends of samples. Bonding points for cables were inserted for the electrical tests.

2.3 Microstructure characterization, electrical and mechanical properties measurements

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A computerized tomography scan (CT, GE phoenix v|tome|x s) was used to exhibit the morphology condition of LATP composite samples before and after mechanical tests.

The cyclic voltammetry (CV) test and electrochemical impedance spectra (EIS) were measured at room temperature by an electrochemical workstation (Vertex, IVIUM TECHNOLOGIES) for the LATP composite samples without and under mechanical load. The measurements were carried out at voltage range of CV was 0.0-0.5V and in different scan rates. The EIS was carried out for all the measurements in the frequency range from 1 MHz to 1 Hz with voltage amplitude of 10mV. Two kinds of samples were analyzed: LATP embedded into composite materials after DP-RTM process called LATP-C samples and composite sample using the same laminates without LATP called reference samples.

Mechanical properties were acquired by fou-points-bending test and tensile test with a universal testing machine (Zwick 1484). Both of the tests were conducted at a rate of 1 mm/min with a pre-load at 5 N to ensure that the sample was under flat condition. A 20 kN load cell was used as well as a transducer. The bending force and deformation were recorded by the software Test-Expert II V3.31 (Zwick).

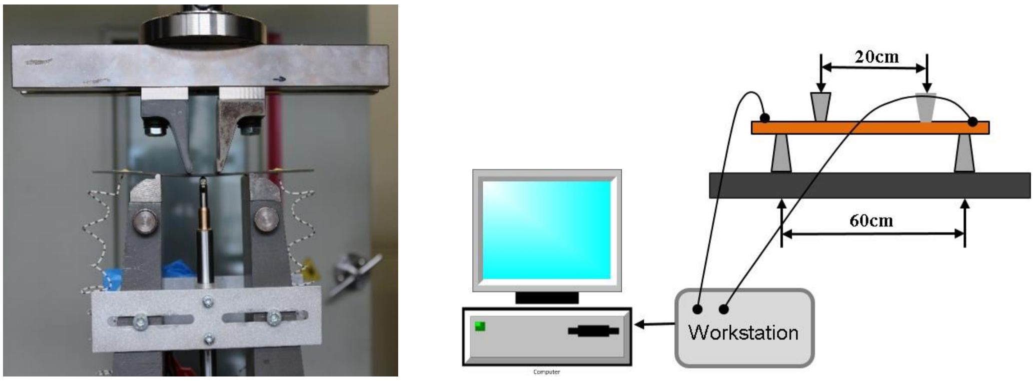

Figure 2. (a) universal testing machine for four point bending tests; (b) sample is connected to electrochemical workstation

Coupling tests were realized by combining mechanical test samples with the electrochemical workstation. A schematic picture of test set-up is showen in Fig.2. A step bending load was used with an interval as 5 N, therefore the static electrical properties were tested under the bending loads as 10N, 15N, 20N, 25N and 30N.

2.4 Mathematical Formulas

2.4.1 Equations for capacitance calculation:

The capacitance is calculated by the CV curve, in which the current is detected responding to voltage change.

Capacitance: $C = \frac{Q}{U} = \frac{1}{\tau(\Delta V)} \int_{Va}^{Vc} iV dV$

Specific capacitance: $C_m = \frac{C}{m}$

C – Capacitance, F; C_m- Specific capacitance, F/g;
ΔV - the applied potential window (Va to Vc);
τ - Scan rate, mV/s; Q - The capacitor’s charge, C;
Δt- Time of a measurement cycle, total time of charge and discharge;
m – Weight of LATP electrolyte, g.

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2.4.3 Equation for bending strength and Young’s modulus
The bending strength and Young’s modulus are calculated by force and deformation recorded by test machine during 4-points-bending test. The equation is according to DIN EN ISO 14125 with equation 10.

$$\sigma = \frac{FL}{bh^2}$$

$$E_f = \frac{0.21L^3}{bh^3}\left(\frac{\Delta F}{\Delta s}\right)$$

σ - Bending stress, MPa; E_f – Bending modulus, MPa;
Δs – Deviation difference of s'' and s' in the middle of sample, mm;
ΔF – Force difference of F'' and F' according to s'' and s', N;
b – Width of samples; h – Thickness of samples.

3 Results and discussions

The solid electrolyte $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ belongs to ceramic materials. The mechanical properties are therefore like the traditional ceramic: high stiffness but brittle. On the contrary, resins used as matrix are usually more flexible. However they usually don’t possess high Young’s modules without fibre-reinforcements. Thus, it is worth being investigated, how is the mechanical behavior of the combination of two components.

3.1 Mechanical property characterization

Four points bending tests are performed to evaluate the flexural stiffness and strength of the LATP-C as well as flexural failure modes of the LATP power composites. All tests are compared with reference samples without LATP pellets and carried out until catastrophic failure occurred. The Table 1shows that samples with embedded LATP pellets shows similar failure strength compared to reference samples, Young’s modulus increases obviously from 650.5MPa to 858.6MPa. On the other hand, ductility of samples decreases because of the brittleness of LATP solid electrolytes.

Fig 2(a) shows the deflection-bending stress curves of LATP-C and reference samples without solid electrolyte separately. Even though the ceramic has different mechanical behavior as RTM-6, the embedded electrolyte doesn`t change the mechanical behavior of samples. That means the structural supercapacitors maintain the flexible property. On the other side, the additional solid element improves the stiffness of LATP-C.

The failure modes of the LATP-C should also be investigated. Figure 4 show the both sides of LATP-C bending sample, in which flaws and a split can be observed on tensile side and just one fracture is observed on compressive side. Ceramic materials are usually brittle, especially under bending loads. The embedding process performed by DP-RTM injection method makes the composite ‘flexible’. It is uncertain, how deep the cracks moved through, and therefore CT tests are executed to observe the situation of the ceramic inside the bending sample before and after breaking. In Fig 5(c), an obvious crack could be observed on the compressed side. Around the main crack, there exist a large amount of small fractures which could influence the electrical properties. This will be discussed later. From cross-section in Fig 5 we can see, however, the crack doesn´t go through the sample. This indicates the fractures are resisted by resin and fleece.

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Table 1. Comparison of mechanical properties between LATP-C and reference samples

	F_{max} [N]	σ_{4PB} [MPa]	E_{4PB} [MPa]	f_{max4PB} [mm]	ε_{4PB} [%]
Reference	36.8±1.8	93.3±1.0	650.5±32.3	13.2±0.3	19.3±0.9
LATP-C	42.4±1.8	89.3±3.2	858.6±34.4	9.8±0.3	15.8±0.5

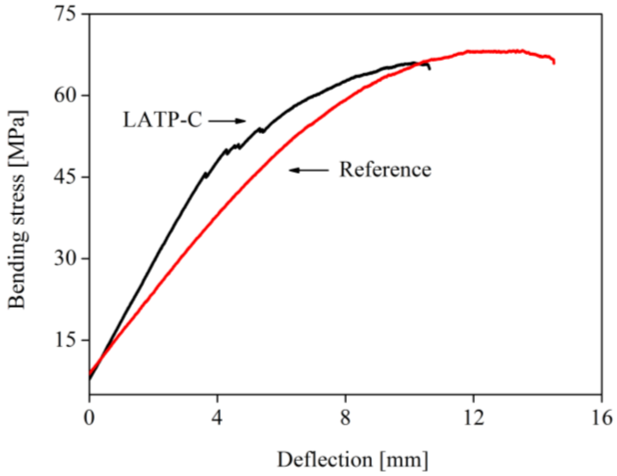

Figure 3 Deflection-bending stress graph of LATP-C and reference

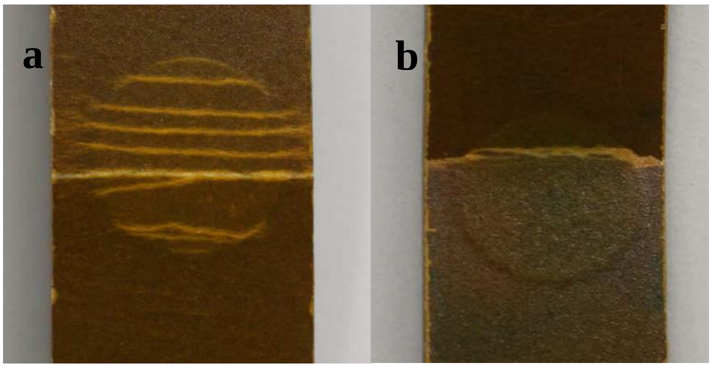

Figure 4 photos of two sides of bending sample after breaking: (a) tensile side; (b) compressive side

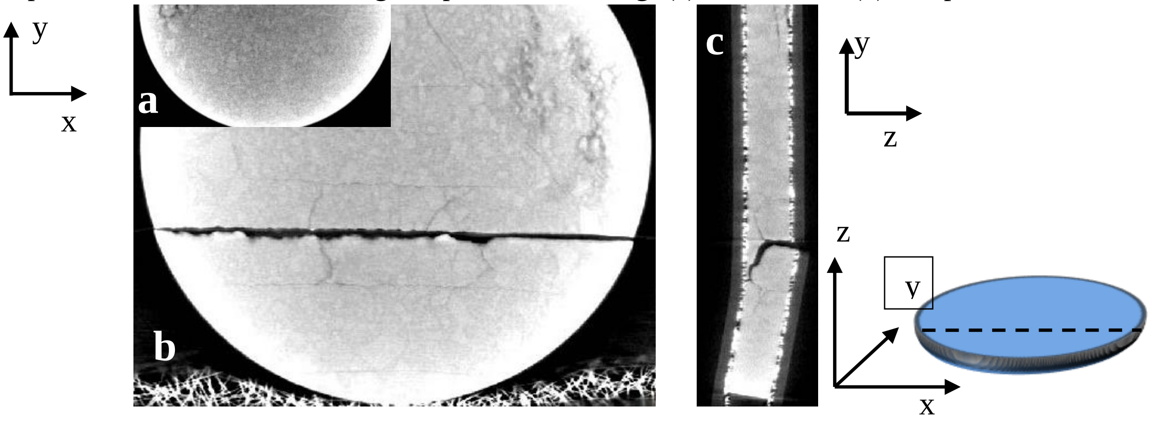

Figure 5. CT photos of LATP before and after breaking: (a) LATP before bending tests; (b) LATP after bending tests; (c) cross-section of LATP after bending tests.

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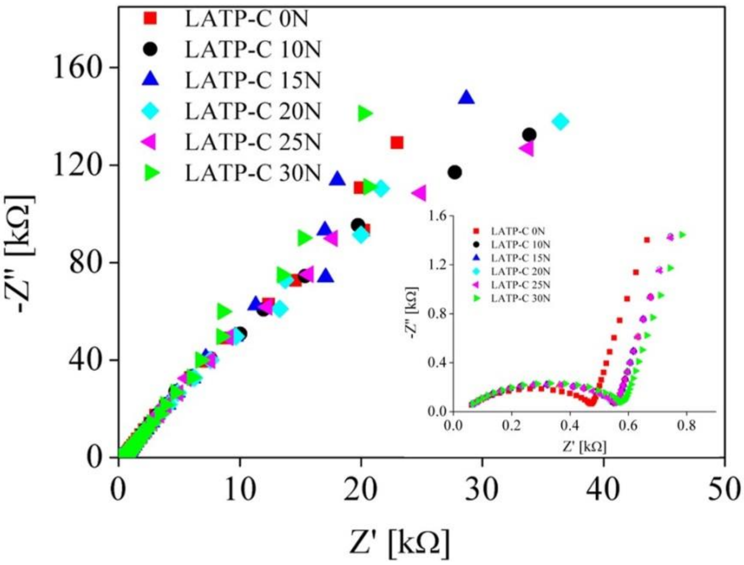
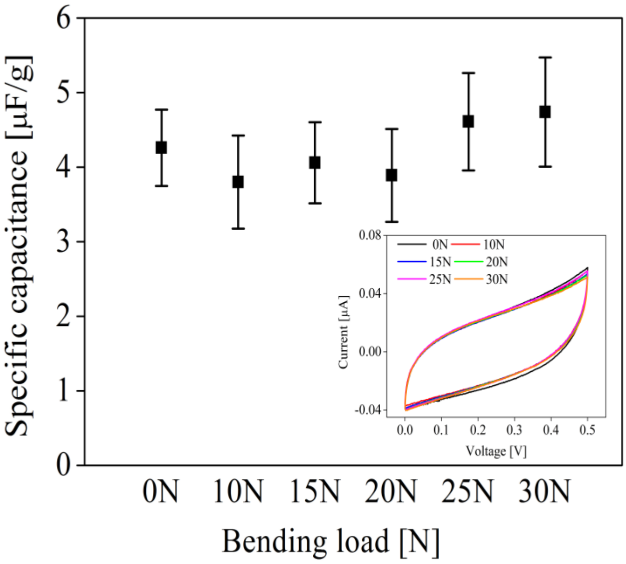
3.2 coupling effect investigation

It is essentially to investigate how the loads influence the electrical properties. Thus, cyclic voltammetry and electrochemical impedance spectroscope are used under different bending loads.

In the high frequency range in EIS Nyquist Plot, the semi-circle has an interception with Z real part at lower frequency range representing the total resistance of the sample. Here, the total resistances increase under bending load indicating a reduction of ionic conductivity. This could be attributed to micro-fractures around the split observed by CT tests. The cracks make a blocking-effect of the Li ions migration which increase the resistance. Those micro-cracks produce during bending loads result in a decrease of ionic conductivity. In low frequency range, curve of oblique line reveals the interface reaction. In Fig 6(a) can see, the resistances of each sample have similar values which mean the leading and cracks don´t strongly influence the ion diffusion at interfaces between electrolyte/electrode/collector.



(a)



(b)

Figure 6. Electrical properties of LATP-C: (a) Nyquist plots of LATP-C under bending loads; (b) capacitances under different bending loads.

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Cyclic voltammetry curves shown in Fig 6(c) reveal the capacitor behavior of LATP-C under different bending loads. No obvious changes have been observed. The capacitances are calculated and presented in Fig 6 (b). The capacitances change irregular under bending loads and the values shift only in a small range. This phenomenon underlies that bending loads don´t have strongly or directly influence on the electricity storage ability of the LATP-C.

4. Conclusions

A new method of producing structural supercapacitors is introduced, which uses NASICON-type $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ as solid electrolyte embedded into composite materials by DP-RTM process. The mechanical properties are characterized by four point bending test. The results show that the embedding element have not dramatically harmed the bending strength and ductility, meanwhile improved the value of Young's Modulus. It indicates that the LATP composite combines the flexibility from resin based system and the stiffness from LATP ceramic. The influence of bending loads on capacitance has also been studied and the results reveal that, the capacitances don't have a regular and obviously change under bending loads. This character brings a benefit for the LATP composite in further application, means here for multifunctional power composites the stable electrical properties are needed.

The study proves the possibility to use $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ solid electrolyte for structural supercapacitor and provides the scientific basis for electrical property improvement in the future research.

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