

# **Development of Sustainable, Multifunctional, Advanced and Smart Hybrid Solid-State Electrolyte for Structural Battery Composites**

---

SHOHEL SIDDIQUE<sup>1,4,\*</sup>, CARLOS FERNANDEZ<sup>2</sup>,  
EYAD ELYAN<sup>1</sup>, MASSIMO DONELLI<sup>3</sup>, DUNCAN GREGORY<sup>4</sup>  
and JAMES NJUGUNA<sup>1</sup>

---

<sup>1</sup>National Subsea Centre, School of Computing, Engineering and Technology, Robert Gordon University, Aberdeen, AB10 7GJ, Scotland, UK

<sup>2</sup>School of Pharmacy, Applied Sciences and Public Health, Robert Gordon University, Aberdeen, AB10 7GJ, Scotland, UK

<sup>3</sup>Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano, 77 - 38123 Trento, Italy

<sup>4</sup>WestCHEM, School of Chemistry, University of Glasgow, Joseph Black Building, Glasgow G12 8QQ, UK

\*Correspondence: [s.a.siddique@rgu.ac.uk](mailto:s.a.siddique@rgu.ac.uk)

## ABSTRACT

The incremental energy demand exacerbates the global warming issues. One of the main triggering factors for this raising global warming is the transportation sector which causes around 30% of the world's emission. However, EU is facing several obstacles to reduce air pollution and greenhouse gas (GHG) emissions caused by the transportation sector. Among these, safety concern in clean technologies is considered the bottleneck to implement emission free technology in transportation sector. Evaluating this obstacle, it was envisaged to run cars with electric power by the rotational power from the electric motor and avoiding the power from internal combustion (IC) engine. Hydrogen (H<sub>2</sub>) powered IC engine emits airborne pollutants like other IC engines. To resolve this issue, H<sub>2</sub> powered fuel cell electric vehicle (FCEV) ensures the clean and emission free transportation dreams into reality. The enormous merits of FCEV including zero emission, faster fueling, noise free drive, economy and higher efficiency (~ 60%) are however restricted mainly due to the storage and safety challenges associated with the H<sub>2</sub>.

The Robert Gordon University supported Catalyst Fund project addresses the existing challenges in designing a safe and smart material development for H<sub>2</sub> storage tank by adopting innovative technologies for: (a) enhancing volumetric mass of H<sub>2</sub> under pressurized condition; (b) a light weight energy storage by further expanding storage of electrochemical energy in structural component without carrying any physical battery; (c) continuous monitoring of damage or leakage due to fatigue/impact; and (d) detection of accumulated moisture hazard well in advance before it causes any unwanted accidents. A composite polymer electrolyte (CPE) as a solid-state electrolyte (SSE) utilizing Li, La, Zr -oxide (LLZO) nanofiber has been synthesized, and the multifunctional property of this new LLZO reinforced CPE is thoroughly under investigation now. The synthesis process and the initial study results are highlighted here. However, the intervening capability of this smart vessel material is the unique characteristic which is missing in the current state-of-the-art technologies. This report initiates this proof of concept in relation to comprehensive integrated power and safety features of H<sub>2</sub> pressure vessel which will overcome the obstacles faced by the current FCEV technology and fostering emission free transportation.

## INTRODUCTION

Hydrogen is an efficient, clean energy carrier with a high specific energy value of 140 MJ/kg. Due to its renewable nature, high energy conversion efficiency, low noise, and environmentally benign, this technology draws the researchers' attention to future sustainable energy sources, mainly in automobile industries. The conformable storage technique for this energy source is the biggest challenge, and based on the technological development, this high-pressure gaseous hydrogen storage tank can be divided into four types, as shown in Figure 1[1]. In addition to these four types, a conformable storage tank consisting of High Energy Coil Reservoir (HECR) attracts researchers' interest due to its light weight, flexibility, non-explosive, and non-fragmenting pressure vessel. Although the liner material development for vehicle applications is highlighted here, a

potential significant cost reduction in material development may make it effective for high pressure ground storage too [2].

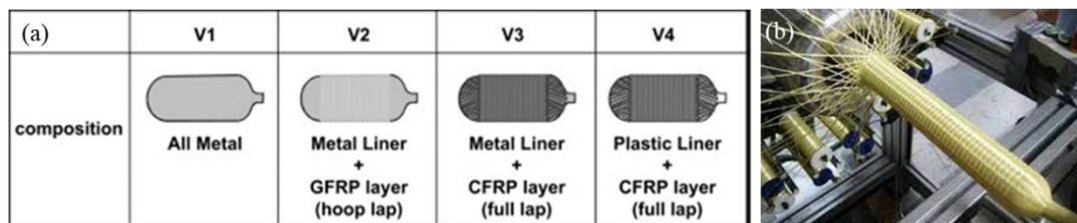


Figure 1: (a) Four types of hydrogen storage tanks<sup>1</sup> and (b) Conformable hydrogen storage vessel<sup>2</sup>.

Bigelow and Lewis in 2018, have demonstrated a Kevlar™ overbraid plastic liner vessel which was able to achieve the pressure target of 3.1X the operating pressure of 700 bar. They also have identified two resins which have excellent hydrogen barrier properties as liner materials of required thickness of 0.06 inches or less. However, a detailed investigation has been carried out by this research group considering 29 resins as potential candidate liner resins. Among them, six resins were selected based on their physical characteristics. Based on the permeability characteristics, three resins were selected at the end such as acetal, EVAL M100 and EVAL F101. However, the test vessel prototypes using these commercially available resins failed the permeability tests for achieve program goals and vehicle applications. A key challenge evolved from liner material selection is that effective hydrogen barrier materials are typically brittle, and it is difficult to process them through the corrugator and be nearly impossible to organise in a stacked form for a larger capacity vessel or high-pressure ground storage facilities.

To follow through these innovative aspects, a sustainable anode material for structural battery composite has been developed and under review for publication now. In that study, a low-cost, abundant and most importantly the raw material sourced from a spent brewery waste (draff) was used to synthesize activated carbon at relatively low temperature ( $\leq 500$  °C) under pyrolytic environment and without using any harsh and toxic chemicals. These draff derived engineered activated carbons (DEACs) are characterized by different physical characterization techniques such as XRD and Raman spectra which revealed the mixed amorphous and graphitic crystalline nature of the DEACs whereas FE-SEM and BET analysis results highlighted the high porous nature of DEACs. The DEACs further showed a promising rate capability and an excellent reversible specific capacity of 43-236 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup> current density after 100 cycles. The sample synthesized at 500 °C using 1:4 pyrolyzed C: KOH showed the highest quality and demonstrates superior electrochemical performance as anode material in a sodium ion battery coin cell with 87% capacity retention over 100 cycles and >99% coulombic efficiency. The detailed results are reported in a separate publication which is under review now. However, the structural integrity of similar fiber reinforced polymer study has been reported previously [3-5], and the electrochemical energy storage investigation is under review now.

Considering all these obstacles mentioned above, this report highlights the promising characteristics of new CPE as structural battery composite (SBC) component to provide multidirectional properties including structural integrity, energy storage, and structural

health monitoring. In summary, there are four parameters which play the vital role in developing a sustainable SBC including high energy density, cycle life, cost and safety features. These four parameters are closely linked with the relation and performances between electrodes and electrolytes of the SBC. It is therefore essentially important to evaluate the stability and charging-discharging mechanisms between electrodes using different electrolytes. However, SSE pose a sustainable solution to replace liquid electrolyte by superseding its performances, cost, environmental and fire hazards.

## METHOD OF APPROACH

A CPE has been synthesized by utilizing the same reactants reported by Li *et al.*, [6]. In their study, garnet  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) nanofiber-incorporated PVDF-HFP has been synthesized, and the morphology and ionic conductivity have been reported. In our study, a simple and a new one pot synthesis process was carried out using same reactants as used by Li *et al.*, in their study. The effect of different calcination temperatures and choice of collectors (aluminium, steel and copper plates) on morphology changes in LLZO nanofibers is reported in this study. The load bearing capacity, smoother and faster Li-ion transport pathways, suppressing Li dendrite growth, better cycling performances and rate capability along with possible a chipless radio-frequency identification-based pervasive crack sensing transducer for structural health monitoring (SHM) relies on structure and morphology of synthesized nanofibers and their dispersion mechanisms in polymer matrix. In the following section, a step-by-step development process of CPE is briefly described.

## MATERIALS

Lithium nitrate ( $\text{LiNO}_3$ ) (99.9%, Sigma-Aldrich), lanthanum nitrate hexahydrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) (99.9%, Sigma-Aldrich), zirconium propoxide ( $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$ ) (70 wt% in 1-propanol, Sigma-Aldrich), dimethylformamide (DMF) (99.9%, Sigma-Aldrich), acetic acid ( $\text{CH}_3\text{COOH}$ ) (99.9%, Sigma-Aldrich), bis(trifluoromethanesulfoneimide) lithium salt (LiTFSI) (99.9%, Sigma-Aldrich), propylene carbonate (PC) (99.9%, Sigma-Aldrich), and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) ( $M_w = 400000$ , Sigma-Aldrich) were used as purchased without further purification.

## SYNTHESIS PROCESS

To prepare the precursor for electrospinning operation, 0.6910 g  $\text{LiNO}_3$ , 1.1188 g  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 0.6550 g  $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$  were mixed thoroughly using a ball mill (200 rpm) followed by dissolving in 7 mL DMF with 2 mL acetic acid and kept stirring magnetically for 30 min. A separate PVP solution (15 wt%) was made using DMF. These two solutions were mixed to form a transparent precursor solution. Electrospinning process was carried out with a voltage of 15 kV, a feeding rate of 2 mL  $\text{h}^{-1}$ , and the distance between the syringe needle and grounded drum collector was 8 cm. The as spun nanofillers were sintered at 500 °C (aluminum plate) and 750 °C (steel and Cu plate) for 4 h in air with a heating rate of 2 °C  $\text{min}^{-1}$ .



Figure 2: Step-by-step synthesis process for developing solid-state electrolyte.

PVDF-HFP and LiTFSI were dissolved in DMF at 2:1 weight ratio and sonicated to form a homogeneous solution followed by adding LLZO at 20 wt% of total weight of PVDF-HFP and LiTFSI. After magnetically stirring for 5 h, the light brown solution was cast onto well dishes. Finally, the CPE membranes were obtained by pouring 200  $\mu\text{L}$  of solution on each cavity followed by further drying at 70  $^{\circ}\text{C}$  under vacuum for 12 h to remove the DMF solvent. The dried CPEs were stored in an inert environment for performing different testing and analyses. The synthesis process is illustrated in Figure 2.

### CHARACTERISATION

The structure of LLZO nanofibers (LLZO-NFs) was investigated using a Zeiss EVO LS10 Scanning Electron Microscope (SEM) with a magnification of 4000X, 4.0 mm working distance (WD) and accelerating potential of 25.00 kV. All the samples were gold-palladium coated using sputter deposition for 2 min prior to the experiment. To determine the composition of samples, energy dispersive x-ray analysis (EDXA) (Oxford Instruments INCA Energy) was carried out.

In Figure 3(a-e), SEM images of the as-spun NFs without calcination and using different collectors and the LLZO-NFs calcined at 500  $^{\circ}\text{C}$  and 750  $^{\circ}\text{C}$  on different collectors (Al, Cu and steel plates) are presented respectively. There is a substantial change in NFs structures is noticeable between Figure 3(a) and 3(b) predominantly the diameter of the NFs and the sharpness of these NFs walls. However, a perforated sponge-like structure is noticeable in Figure 3(c) for LLZO-NFs after calcination at 500  $^{\circ}\text{C}$  on Al foil. A sharp and distinctive regular structure of NFs is noticeable in Figure 3(d) which becomes thicker and underwent coalescence when change in the collector plate from Cu foil to stainless steel plate.

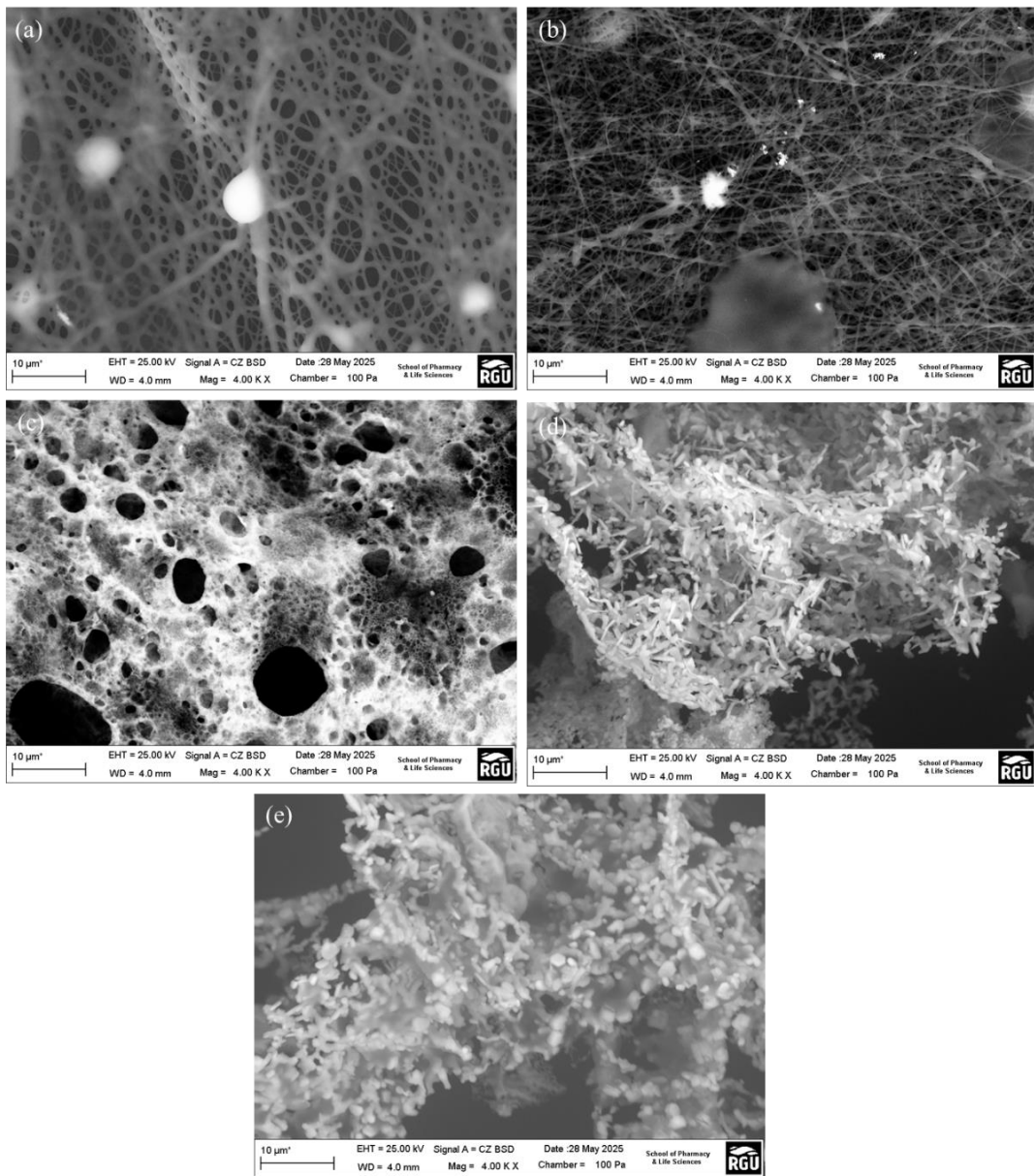


Figure 3: SEM images of (a) LLZO-NFs without calcination on Al foil; (b) LLZO-NFs without calcination on Cu foil; (c) LLZO-NFs calcined at 500 °C on Al foil; (d) LLZO-NFs calcined at 750 °C on Cu foil; and (e) LLZO-NFs calcined at 750 °C on steel foil.

To determine the elemental composition and elucidate the effect of collector material selection and thermal treatment, EDXA was carried out in Figure 4(a-e). A significant reduction in C content is noticeable in LLZO-NFs without calcination on Cu foil compared to that of LLZO-NFs without calcination on Al foil. However, a substantial increase in La and Zr elements are presented in Table I. A huge reduction in C content is noticeable in Table I for all NFs underwent thermal treatment and a substantial rise in La and Zr elements are noticeable. The possible decomposition of polymer content (wt%) may interfere the wt% variation of different elements in different samples and the selection of collector material in electrospinning process may influence the wt% changes in EDXA profile too.

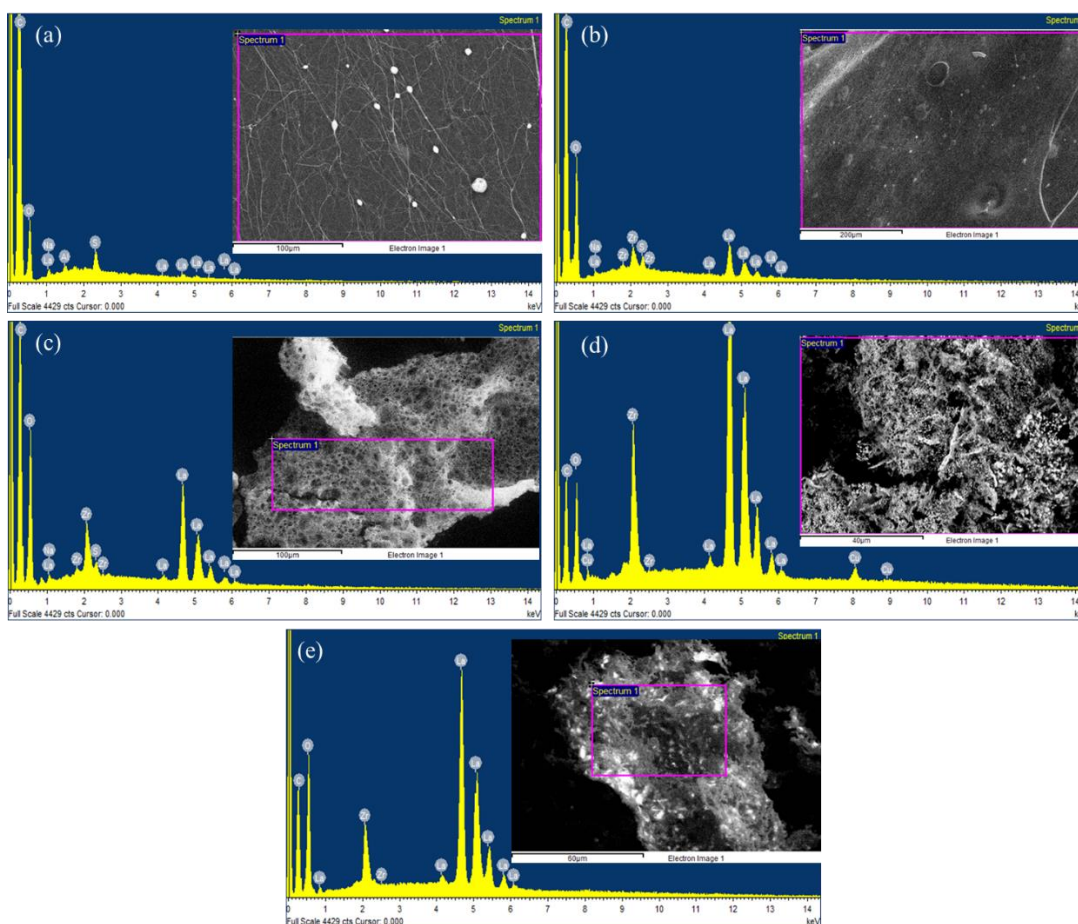


Figure 4: EDXA spectra of (a) LLZO-NFs without calcination on Al foil; (b) LLZO-NFs without calcination on Cu foil; (c) LLZO-NFs calcined at 500 °C on Al foil; (d) LLZO-NFs calcined at 750 °C on Cu foil; and (e) LLZO-NFs calcined at 750 °C on steel foil.

Table I. Elemental composition of different nanofibers synthesized in this study

Element	Weight%				
	LLZO-NFs without calcination on Al foil	LLZO-NFs without calcination on Cu foil	LLZO-NFs calcined at 500 °C on Al foil	LLZO-NFs calcined at 750 °C on Cu foil	LLZO-NFs calcined at 750 °C on steel foil
C	72.36	51.18	43.13	16.96	20.26
O	24.94	35.27	29.12	10.96	21.34
Na	0.47	0.37	0.37	0	0
Al	0.25	0	0	0	0
S	1.02	0.7	0.51	0	0
La	0.96	9.87	22.01	57.52	50.99
Zr	0	2.61	4.86	12.23	7.4
Cu	0	0	0	2.34	0
Totals	100	100	100	100	100

## CONCLUSION

A simple garnet-type ceramic reinforced CPEs were manufactured using electrospinning followed by thermal treatment. Incorporation of LLZO-NFs in polymer matrix has shown different characteristics in terms of morphology structure changes and variation of elemental composition too. It is expected from this study that NFs synthesizing using Cu-foil at 750 °C may bring improvement in load bearing capacity, electrochemical energy storage performances and structural health monitoring study of the targeted SBC development. This study is a key milestone in adaptation of SSE in SBC to facilitate mechanical strength improvement, sustainable energy storage system design and most importantly monitoring the structural health condition in continuous and real time approach.

## ACKNOWLEDGEMENT

This work was supported by the Catalyst Fund - Robert Gordon University [grant number RG/CF/2423285] and Scotland's Comprehensive Hydrogen Storage Testing Facility <https://www.hy-one.co.uk/> [grant number EETF/HIS/ APP/007]. We would like to thank Scottish Government for supporting in this study through HyOne project. We would also like to thank Dr Anil Prathuru, Mr Allan MacPherson, Mr Benjamin Bird, Mr David Howie, Emily Hunter and Mr Patrick Kane for their support in synthesizing and analyses set-up.

## REFERNCES

- [1] Su Y, Lv H, Zhou W, Zhang C. Review of the Hydrogen Permeability of the Liner Material of Type IV On-Board Hydrogen Storage Tank. *World Electric Vehicle Journal*. 2021 Aug 22;12(3):130.
- [2] Bigelow E, Lewis M. Conformable Hydrogen Storage Pressure Vessel. Center for Transportation and the Environment, Atlanta, GA (United States); 2018 Jul 6.
- [3] Jenkins P, Siddique S, Khan S, Usman A, Starost K, MacPherson A, Bari P, Mishra S, Njuguna J. Influence of reduced graphene oxide on epoxy/carbon fiber-reinforced hybrid composite: flexural and shear properties under varying temperature conditions. *Advanced Engineering Materials*. 2019 Jun;21(6):1800614.
- [4] Siddique S, Novak A, Guliyev E, Yates K, Leung PS, Njuguna J. Oil-Based Mud Waste as a Filler Material in LDPE Composites: Evaluation of Mechanical Properties. *Polymers*. 2022 Apr 2;14(7):1455.
- [5] Siddique S, Yates K, Matthews K, Csetenyi LJ, Njuguna J. Oil-based mud waste reclamation and utilisation in low-density polyethylene composites. *Waste Management & Research*. 2020 Dec;38(12):1331-44.
- [6] Li Y, Zhang W, Dou Q, Wong KW, Ng KM. Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> ceramic nanofiber-incorporated composite polymer electrolytes for lithium metal batteries. *Journal of Materials Chemistry A*. 2019;7(7):3391-8.