



# Article The Conversion of Li<sub>2</sub>SnO<sub>3</sub> Li-Ion Hybrid Supercapacitors from Pastes Containing LiCl-SnCl<sub>2</sub> Liquid Precursors Using an Atmospheric-Pressure Plasma Jet

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**Abstract:** We fabricate lithium tin-based oxide  $Li_2SnO_3$  on carbon cloth from a gel-state precursor containing LiCl and  $SnCl_2 \cdot 2H_2O$  using a nitrogen atmospheric-pressure plasma jet (APPJ). APPJ treatment provides both a high-temperature environment for the conversion of precursor into  $Li_2SnO_3$  and nitrogen plasma reactive species for electrode surface modification. Here, the best electrochemical performance for the  $Li_2SnO_3$  Li-ion hybrid supercapacitors (Li–HSCs) is achieved with 480 s of APPJ processing. The areal capacity of the 480 s APPJ-processed  $Li_2SnO_3$  Li–HSCs reached 46.113 mC/cm<sup>2</sup>. The results indicate that APPJ is an effective tool for the rapid conversion processing of  $Li_2SnO_3$  electrodes for Li–HSCs.

**Keywords:** atmospheric pressure plasma (APP); Li-ion hybrid supercapacitors (Li-HSCs); flexible electronics; lithium tin oxide ( $Li_2SnO_3$ )

# 1. Introduction

As electrical energy storage (EES) systems progress, the focus of numerous researchers has turned to supercapacitors (SCs) and lithium-ion batteries (LIBs). These emerging technologies are driving a revolution across various domains, from small-scale portable electronics to hybrid electric vehicles [1–4]. Although LIBs have high energy density, their power density is relatively low [5,6]. By contrast, SCs have a much higher power density and a faster charging rate than LIBs, and thus can perfectly compensate for the shortcomings of LIBs [7,8]. Therefore, Li-ion hybrid SCs (Li-HSCs), which combine the advantages of SCs and LIBs, have become attractive for use in next-generation EES devices [9,10].

The energy storage mechanism of supercapacitors (SCs) can be categorized as electrical double-layer capacitance (EDLC) and pseudocapacitance (PC). EDLC is mainly related to accumulating charges on the chemical reactive surface, and PC is related to reversible redox reactions [11–13]. Li-HSCs need high-performance materials, and a high concentration of Li<sup>+</sup> ions can offer intercalation and deintercalation charge storage mechanisms [14,15]. Various Li-containing materials, such as Li<sub>2</sub>SnO<sub>3</sub>, LiMn<sub>2</sub>O<sub>4</sub>, Li<sub>2</sub>MnO<sub>3</sub>, Li<sub>2</sub>MnSiO<sub>4</sub>, and Li<sub>5</sub>FeO<sub>4</sub>, are being rapidly developed for Li-HSCs because they are abundant, cost-effective, less polluting, and less harmful to humans [16–18]. Among these, Li<sub>2</sub>SnO<sub>3</sub> has proven



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to be a promising material with great electrochemical performance.  $Li_2SnO_3$  crystalizes in a monoclinic layered structure with space group C2/c and consists of eight molecules per unit cell. Patterson and difference Fourier maps have been used to determine the atomic positions of all Li<sup>+</sup>, Sn<sup>4+</sup> and O<sup>2-</sup> in a structure [19]. Because Li<sub>2</sub>SnO<sub>3</sub> is sintered in high-temperature conditions, the medium-temperature APPJ technology can be applied.

Unlike low-pressure plasma (LPP), the atmospheric-pressure plasma jet (APPJ) can operate at regular atmospheric pressures without requiring vacuum systems. It contains highly reactive species and a high energy density, delivering rapid and cost-effective processing technology. The typical issues with APPJ technology, such as continuous arcing, instability, and high breakdown voltage problems, have been resolved, and the technology has become a suitable industrial processing method [20–22]. Practical applications, such as material surface modification, sterilization and bacteria inactivation, rapid annealing, and the rapid processing of transition metal oxides, widely employ APPJs in various fields [23,24]. Material processing utilizing medium-temperature atmospheric-pressure plasma jets (APPJs) relies on the combined impact of heat and reactive species from the plasma. This synergy results in the generation of practical medium-to-high temperatures within the plasma, along with diverse charge densities [25]. Among the many kinds of gases available, nitrogen is abundant, economical, and environmentally friendly. In previous studies, nitrogen APP has been proven to be highly reactive to carbonaceous materials. When carbonaceous materials were treated by nitrogen APPJ in our experiment, the screenprinted pastes containing ethyl cellulose on carbon cloth were completely removed within ~90 s, and the  $Li_2SnO_3$  crystal was sintered within about 300 s. These results can be attributed to the synergetic effect of reactive plasma species and heat. In the present study, rapidly APPJ-processed Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs are investigated.

#### 2. Experimental

#### 2.1. Preparation of LiCl-SnCl<sub>2</sub>·2H<sub>2</sub>O Pastes

For the preparation of the LiCl-SnCl<sub>2</sub>·2H<sub>2</sub>O pastes, 0.5325 g of SnCl<sub>2</sub>·2H<sub>2</sub>O (purity: 99%, Aldrich, Munich, Germany), 0.1 g of anhydrous LiCl (purity: 99%, Alfa Aesar, Ward Hill, MA, USA), and 3.245 g of terpineol (anhydrous, #86480, Aldrich) were mixed with an ethanolic solution containing 1.75 g of 10 wt% ethyl cellulose (#46070, Sigma, Munich, Germany), 2.25 g of 10 wt% ethyl cellulose (#46080, Sigma), and 1.5 g of ethanol. The mixture was stirred well at 900 rpm for 24 h. The stirred mixture was then subjected to a rotary evaporator at 55 °C for 6 min to condense the pastes.

#### 2.2. Fabrication of Li-HSCs

Figure 1a shows the fabrication process of the Li<sub>2</sub>SnO<sub>3</sub> electrode. The LiCl-SnCl<sub>2</sub> pastes were applied to the carbon cloth (1.5 cm  $\times$  2 cm) through screen printing, repeated three times, and subsequently dried in an oven at 100 °C for 10 min. The screen-printed electrodes were then processed using a nitrogen APPJ. The nitrogen flow rate of the APPJ was 46 slm. The APPJ processing times were 0, 5, 30, 90, 180, 300, and 480 s for converting the LiCl-SnCl<sub>2</sub> precursor into Li<sub>2</sub>SnO<sub>3</sub> and for burning out the excess binders on the electrodes. The electrodes were then used for the Li-HSCs. Figure 1b shows the carbon cloth temperature, measured using a K-type thermocouple. The temperature rapidly increased to 500 °C and then gradually increased to 620 °C after the APPJ was turned on. Other detailed APPJ operation parameters were described in a previous study [26]. Lastly, with a three-electrode configuration in a 1-M Li<sub>2</sub>SO<sub>4</sub> liquid electrolyte, the Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs were used as the working electrode, and the reference and counter electrodes were represented by Ag/AgCl and Pt electrodes, respectively [27].



**Figure 1.** (a) Fabrication process of the Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs. (b) Evolution of carbon cloth temperature during APPJ processing.

#### 2.3. Characterizations of Li<sub>2</sub>SnO<sub>3</sub> and Li-HSCs

A Sindetake Model 100SB goniometer measured the water contact angle of Li<sub>2</sub>SnO<sub>3</sub> onto carbon cloth. The electrode surface morphology was inspected using a JEOL JSM-7800 F Prime scanning electron microscope (SEM) (Tokyo, Japan), equipped with the capacity to perform energy-dispersive X-ray spectroscopy (EDS). The crystallinity of Li<sub>2</sub>SnO<sub>3</sub> was examined using a Bruker D2 Phaser X-ray diffractometer (Billerica, MA, USA) with a Cu-K $\alpha$  source. Surface chemical components were analyzed using Thermo VG Scientific Sigma Probe X-ray photoelectron spectroscopy (XPS, Waltham, MA, USA) with an Al-K $\alpha$  X-ray source. Cyclic voltammetry (CV) and galvanostatic charging/discharging (GCD) were performed using a Metrohm Autolab PGSTAT204 electrochemical workstation (Utrecht, The Netherlands), with potential windows of 0–0.8 V for both, potential scan speeds ranging from 2 to 200 mV/s for CV, and constant currents of 4, 2, 1, and 0.5 mA for GCD.

#### 3. Results

#### 3.1. Water Contact Angle

Figure 2 shows the water contact angle of the as-deposited LiCl-SnCl<sub>2</sub>·2H<sub>2</sub>O precursor on carbon cloth and those seen after APPJ treatment. Figure 2a shows that the pristine carbon cloth exhibited hydrophobic characteristics with a high contact angle of 133.18°; this value was consistent with our previous findings. However, the as-deposited samples and those after APPJ treatment were hydrophilic. Figure 2b shows that the water droplets completely penetrated the as-deposited sample surface within about 12 s. By contrast, it penetrated the APPJ-processed samples immediately after the droplet was dispensed. The enhanced hydrophilicity of the  $Li_2SnO_3$  electrode surface could be attributed to the hydrophilic surface functional group containing nitrogen and oxygen conferred by the APPJ process in a nitrogen working environment [28,29]. The improved hydrophilicity promoted contact between the  $Li_2SnO_3$  Li-HSCs electrode surface and the 1-M  $Li_2SO_4$ liquid electrolyte, delivering better electrochemical performance [30].



**Figure 2.** Water contact angles of (**a**) pristine carbon cloth and  $\text{Li}_2\text{SnO}_3$  electrodes. This was processed by APPJ for (**b**) 0 s, (**c**) 5 s, (**d**) 30 s, (**e**) 90 s, (**f**) 180 s, (**g**) 300 s, and (**h**) 480 s.

## 3.2. SEM

Figure 3 shows SEM images with a magnification rate  $(5000 \times)$ . Figure 3b shows that the ethyl cellulose mostly wrapped the as-deposited LiCl-SnCl<sub>2</sub>·2H<sub>2</sub>O pastes. The thermal decomposition temperature of ethyl cellulose is about 312 °C [31]; therefore, it is burned out during APPJ treatment (620 °C). The attachment of the residual ethyl cellulose to the electrode surface hinders the ion adsorption and desorption capacity of the liquid electrolyte [32]. Figure 3h shows that ethyl cellulose was completely removed after APPJ processing time of 480 s; however, the carbon fibers became rough due to the plasma treatment. Figure 4 shows SEM images with a higher magnification rate (50,000×). As the APPJ processing time increased, we observed that a large amount of Li<sub>2</sub>SnO<sub>3</sub> crystals had grown on the carbon fibers. Figure 4h shows that the 480 s APPJ-processed sample exhibited the best crystallinity. The results demonstrate that high-temperature nitrogen APPJ treatment can be used for the rapid conversion of Li<sub>2</sub>SnO<sub>3</sub>.



**Figure 3.** SEM images ( $5000 \times$ ) of (**a**) pristine carbon cloth, Li<sub>2</sub>SnO<sub>3</sub> electrodes processed by APPJ for (**b**) 0 s, (**c**) 5 s, (**d**) 30 s, (**e**) 90 s, (**f**) 180 s, (**g**) 300 s, and (**h**) 480 s.



**Figure 4.** SEM images  $(50,000 \times)$  of (**a**) pristine carbon cloth, Li<sub>2</sub>SnO<sub>3</sub> electrodes processed by APPJ for (**b**) 0 s, (**c**) 5 s, (**d**) 30 s, (**e**) 90 s, (**f**) 180 s, (**g**) 300 s, and (**h**) 480 s.

#### 3.3. XRD

Figure 5 shows the XRD patterns of Li<sub>2</sub>SnO<sub>3</sub> electrodes when processed by APPJ for 0 s, 5 s, 30 s, 90 s, 180 s, 300 s, and 480 s. Figure 5a shows the obvious diffraction peaks at  $2\theta = 26^{\circ}$ , which can be attributed to the presence of the carbon cloth [33]. The intensity of the diffraction peak was particularly weak in the as-deposited sample because of the covering of the electrode surface with unburned ethyl cellulose. Furthermore, additional diffraction peaks corresponding to the (200) lattice plane of Li<sub>2</sub>SnO<sub>3</sub> were found at  $2\theta = 34.1^{\circ}$  [34]. These peaks could be attributed to a monoclinic-layered structure. Figure 5b shows a magnified view of the XRD pattern of the (200) Li<sub>2</sub>SnO<sub>3</sub> lattice plane. No significant peaks were observed in the samples after APPJ processing for 0 s, 5 s, 30 s, 90 s, and 180 s. By contrast, diffraction peaks were observed in the 300 s and 480 s APPJ-processed samples. This phenomenon demonstrates that the monoclinic Li<sub>2</sub>SnO<sub>3</sub> gradually grew on the carbon cloth fiber surface due to the high temperature of the nitrogen APPJ processing and its presence increased with processing time. Furthermore, the better crystallinity of Li<sub>2</sub>SnO<sub>3</sub> helped to improve the electrochemical performance of Li-HSCs. These XRD results of crystallinity are also in good agreement with the SEM results.



**Figure 5.** (a) Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs XRD patterns. (b) Magnified view of XRD patterns of the (200) lattice plane of Li<sub>2</sub>SnO<sub>3</sub>.

#### 3.4. XPS

Figure 6 shows the XPS results of  $Li_2SnO_3$  electrodes processed by APPJ. The chemical configurations of C1s, O1s, and Sn3d, as well as Li1s XPS spectra of  $Li_2SnO_3$ , were identified. Figure S1 shows the  $Sn3d^{5/2}$  spectrum, which can be deconvoluted into three peaks at 485.8, 486.9, and 487.6 eV, corresponding to  $Sn^{0+}$ ,  $Sn^{2+}$ , and  $Sn^{4+}$  [35,36]. Table S1 shows the relative bonding contents obtained from XPS analysis of  $Sn3d^{5/2}$ . The highest  $Sn^{4+}$  bonding content arose in the APPJ 480 s case, which indicates that most of the precursors on the electrode surface were transformed into  $Li_2SnO_3$  crystals via APPJ. This is in good agreement with the SEM and XRD results. Figure S2 shows the Li1s spectra at 54.5–55.5 eV, which proves that the electrode surface really contained Li elements [37].



**Figure 6.** XPS survey spectra of Li<sub>2</sub>SnO<sub>3</sub> electrodes processed by APPJ for (**a**) 0 s, (**b**) 5 s, (**c**) 30 s, (**d**) 90 s, (**e**) 180 s, (**f**) 300 s, and (**g**) 480 s.

#### 3.5. CV of Li-HSCs s

Figure 7 shows the areal capacity of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs under various APPJ processing times. The CV results were conducted using potential scan rates of 200, 20, and 2 mV/s within a three-electrode system. The areal capacity  $Q_c$  (mC/cm<sup>2</sup>) was calculated using Equation (1):

$$Q_C = \frac{S}{2 \times A \times v} \tag{1}$$

where *A* is the screen-printed area of the electrode (1.5 cm  $\times$  2 cm), *v* is the potential scan rate, and *S* is the total area enclosed by the CV curve. Figure S3 shows the CV results measured in the two-electrode symmetric system, and Table 1 shows that the 480 s APPJ-processed Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs had the largest area of those enclosed by the CV curve, with

a corresponding areal capacity of 46.113 mC/cm<sup>2</sup> at a scan rate of 2 mV/s. As the APPJ processing time increased, the areal capacity gradually increased because of the removal of ethyl cellulose and the successful conversion of  $Li_2SnO_3$  crystals. The results also showed that the areal capacity was higher under a low potential scan rate owing to the fact that Li-ions of 1-M  $Li_2SO_4$  liquid electrolyte were available for sufficient time to complete the redox reactions and intercalate/deintercalate effectively on the electrode surface [38].



**Figure 7.** CV curves for Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs under potential scan rates of (**a**) 200 mV/s, (**b**) 20 mV/s, and (**c**) 2 mV/s.

<b>Table 1.</b> Theat capacity of Lifono's Liftbes calculated based on C v result	Table 1. Areal car	pacity of Li <sub>2</sub> SnO <sub>3</sub>	Li-HSCs calculated	based on CV result
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Areal Capacity (mC/cm <sup>2</sup> )				
Potential Scan Rate	200 mV/s	20 mV/s	2 mV/s	
As-deposited	0.143	0.079	0.146	
APPJ 5 s	2.309	7.810	5.418	
APPJ 30 s	6.479	19.165	23.401	
APPJ 90 s	7.507	27.871	33.499	
APPJ 180 s	3.627	24.542	36.076	
APPJ 300 s	5.182	28.905	46.017	
APPJ 480 s	7.309	32.611	46.113	

#### 3.6. Trasatti Plots of Li-HSCs

Trasatti analysis can assess the respective contributions of EDLC and PC. Its theoretical framework revolves around surface charges and diffusion-controlled charges. We can analyze the differences in the contribution of surface charge (Qout), EDLC, diffusioncontrolled charge (Qin), and PC by applying various scan rates in the CV test (Figure 8a–g). As the scan rate decreases towards zero, sufficient time is provided for the enhanced diffusion of charges across both the inner and outer surfaces of the electrode, thereby attaining maximum capacity. By contrast, when the scan rate approaches infinity, only the surface charges contribute to the charge storage mechanism. Figure 8h shows the  $Q_{out}$ , the intercept of the vertical axis (when  $v^{-1/2} = 0$ , the scanning rate is infinity), in the plot of Qc versus the horizontal axis  $v^{-1/2}$ . Figure 8i shows the  $Q_{total}$  (=  $Q_{in} + Q_{out}$ ), the intercept of the fitted line, and the vertical axis 1/Qc (when  $v^{1/2} = 0$ ). Table 2 shows the calculated capacity contribution of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs. It exhibited the highest PC in the APPJ 480 s case. As PC is mainly related to redox reactions, the results can be explained by the formation of better  $Li_2SnO_3$  crystals [39]. This outcome was also in good agreement with the previous SEM and XRD analyses. Further, we observed a decrease in EDLC values with 300 s and 480 s APPJ processing. Given that EDLC is mainly related to surface charges, this outcome can be attributed to the damage to the material by the high-temperature APPJ during extended processing periods.



**Figure 8.** (a–i) CV curves of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs under potential scan rates of 2–200 mV/s in Trasatti plots of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs: (e)  $Q_c$  versus  $v^{-1/2}$ ; (f) 1/  $Q_c$  versus  $v^{1/2}$ .

<b>Table 2.</b> Capacity contribution of Li	i <sub>2</sub> SnO <sub>3</sub> 1	Li-HSCs as anal	yzed usi	ng Trasatti meth	ıod.
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	Q <sub>total</sub> (mC/cm <sup>2</sup> )	Q <sub>out</sub> (mC/cm <sup>2</sup> )	Q <sub>in</sub> (mC/cm <sup>2</sup> )
As-deposited	1.346	0.059	1.288
APPJ 5 s	1.983	1.064	0.919
APPJ 30 s	30.619	13.277	17.341
APPJ 90 s	51.619	13.132	38.487
APPJ 180 s	52.247	20.841	31.406
APPJ 300 s	79.808	22.658	57.150
APPJ 480 s	85.324	17.567	67.757

# 3.7. GCD of Li-HSCs

Figure 9 shows the GCD results of  $Li_2SnO_3$  Li-HSCs processed by APPJ for 0 s, 5 s, 30 s, 90 s, 180 s, 300 s, and 480 s under constant currents of 4, 2, 1, and 0.5 mA. Equation (2) was used to calculate the areal capacity Qc ( $\mu$ A h/cm<sup>2</sup>):

$$Q_c = \frac{I \times T}{A} \tag{2}$$

where *A* is the area of the electrode (1.5 cm  $\times$  2 cm), *I* is the charging/discharging current, and *T* is the discharging time [31]. Figure 9 and Table 3 show the GCD results in the three-electrode system. Figure S4 and Table S3 show the GCD results in the two-electrode symmetric system. Together, these findings demonstrate that the Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs processed by APPJ for 480 s had the best performance in terms of areal capacity out of the

two types of systems. These results also agree with the CV results. Additionally, the change in the slope of the GCD curve under constant currents of 1 and 0.5 mA indicates that  $Li_2SnO_3$  performed a more obvious redox reaction for a low-discharging current in the three-electrode system [40]. This phenomenon was not observed in a two-electrode system because of the measurement inaccuracy caused by polarization currents. Figure 9h shows the Ragone plot, analyzed based on the GCD results. Ragone plots were used to evaluate the energy and power density of the  $Li_2SnO_3$  Li-HSCs. The energy density  $E_A$  and power density  $P_A$  are, respectively, calculated using Equations (3) and (4):

$$E_A = \frac{C_A \times \Delta V^2}{7.2} \tag{3}$$

$$P_A = \frac{3.6 \times E_A}{T} \tag{4}$$

where  $C_A$  is the areal capacitance obtained from the GCD results,  $\Delta V$  is the scanning potential window, and *T* is the discharging time. Table 4 shows that the 480 s APPJ-processed Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs exhibited the best energy density of 5.59 µWh/cm<sup>2</sup> under a discharging current of 0.25 mA. This result indicates that the energy density increased with an increase in APPJ treatment time. Tables 4 and 5 list the energy density and power density of the fabricated Li-HSCs.



**Figure 9.** GCD curves of (**a**) untreated Li-HSCs and Li-HSCs processed by APPJ for (**b**) 5 s, (**c**) 30 s, (**d**) 90 s, (**e**) 180 s, (**f**) 300 s, and (**g**) 480 s. (**h**) Ragone plot analyzed based on GCD results.

Areal Capacity (µA h/cm <sup>2</sup> )				
Charging/ Discharging Current	4 mA	2 mA	1mA	0.5 mA
As-deposited	0.362	0.179	0.176	0.203
APPJ 5 s	0.379	0.194	0.217	0.252
APPJ 30 s	1.426	2.190	3.089	3.819
APPJ 90 s	3.762	4.725	5.628	6.095
APPJ 180 s	4.138	6.374	8.099	8.948
APPJ 300 s	6.142	7.706	8.922	9.374
APPJ 480 s	5.688	7.333	8.696	9.376

Table 3. Areal capacity of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs calculated based on GCD results.

 Table 4. Energy density of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs calculated based on GCD results.

Energy Density (µWh/cm <sup>2</sup> )				
Charging/ Discharging Current	4 mA	2 mA	1mA	0.5 mA
As-deposited	0.0328	0.0676	0.0756	0.1012
APPJ 5 s	0.0348	0.0684	0.1352	0.1848
APPJ 30 s	0.0804	0.1092	0.1376	0.2728
APPJ 90 s	2.1476	2.6748	3.0916	3.3972
APPJ 180 s	3.4320	3.9112	4.2036	4.4404
APPJ 300 s	3.8684	4.3696	4.7004	4.8816
APPJ 480 s	4.7104	5.1388	5.4064	5.5892

Table 5. Power density of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs calculated based on GCD results.

The Power Density (mW/cm <sup>2</sup> )				
Charging/ Discharging Current	4 mA	2 mA	1mA	0.5 mA
As-deposited	0.1216	0.2514	0.2856	0.3772
APPJ 5 s	0.1116	0.2350	0.2078	0.1221
APPJ 30 s	0.0752	0.0332	0.0149	0.0119
APPJ 90 s	0.7612	0.3774	0.1831	0.0929
APPJ 180 s	1.1059	0.4091	0.1730	0.0827
APPJ 300 s	0.8398	0.3780	0.1756	0.0868
APPJ 480 s	1.1043	0.4672	0.2072	0.0994

## 3.8. Stability of Li-HSCs

Figure 10 and Table 6 show the results of the 1000-cycle CV stability test in the threeelectrode system (potential scan rate = 20 mV/s) of the 480 s APPJ-processed  $Li_2SnO_3$ Li–HSCs. The areal capacity of the electrode decreased to 24.72% of the initial performance after 1000 cycles. By contrast, Figure S5 and Table S4 show the results in the two-electrode system; the areal capacity of the electrode decreased to 63.56%. The differences between these two measurement results can be attributed to the polarization current generated by the two-electrode system during the measurement process, resulting in a larger current value being measured and the distortion of the capacity retention rate [41].

Table 6. Capacity retention rate of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs.

Cycle Number	Capacity Retention (%)
2	100
100	59.04
200	50.38



Table 6. Cont.

Figure 10. Representative cycling stability curves of Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs processed by APPJ for 480s.

## 4. Conclusions

In this study, we screen-printed LiCl-SnCl<sub>2</sub>·2H<sub>2</sub>O pastes on carbon cloth and converted the material using nitrogen APPJ to fabricate Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs. SEM, XRD, and XPS analyses confirmed the success of the conversion into Li<sub>2</sub>SnO<sub>3</sub>. CV and GCD tests were used to characterize electrochemical performance. The optimal APPJ processing time for Li<sub>2</sub>SnO<sub>3</sub> SCs was 480 s. The 480 s APPJ-processed Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs exhibited an areal capacity of 46.113 mC/cm<sup>2</sup>, which was far superior to that of the as-deposited sample. Through the above series of tests, we confirmed that high-temperature nitrogen APPJ processing was an efficient and rapid method for fabricating Li<sub>2</sub>SnO<sub>3</sub> Li-HSCs electrodes.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/jcs8050189/s1, Figure S1: O1s fine-scan spectra of Li2SnO3 electrodes processed by APPJ; Table S1: Bonding contents obtained from XPS analysis of Sn3d5/2; Figure S2: Li1s fine-scan spectra of Li2SnO3 electrodes processed by APPJ; Figure S3: CV curves for Li2SnO3 Li-HSCs under potential scan rates; Table S2: Areal capacity of Li2SnO3 Li-HSCs calculated based on CV results in two-electrode symmetric system; Figure S4: GCD curves of (a) untreated Li-HSCs and Li-HSCs processed by APPJ; Table S3: Areal capacity of Li2SnO3 Li-HSCs calculated based on GCD results in two-electrode symmetric system; Figure S5: Representative cycling stability curves of Li2SnO3 Li-HSCs processed by APPJ for 480s in two-electrode symmetric system; Table S4: Capacity retention rate of Li2SnO3 Li-HSCs in two-electrode symmetric system.

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#### References

- 1. Soltani, M.; Ronsmans, J.; Kakihara, S.; Jaguemont, J.; Van den Bossche, P.; Van Mierlo, J.; Omar, N. Hybrid battery/lithium-ion capacitor energy storage system for a pure electric bus for an urban transportation application. *Appl. Sci.* **2018**, *8*, 1176. [CrossRef]
- Khan, K.; Tareen, A.K.; Aslam, M.; Mahmood, A.; Zhang, Y.; Ouyang, Z.; Guo, Z.; Zhang, H. Going green with batteries and supercapacitor: Two dimensional materials and their nanocomposites based energy storage applications. *Prog. Solid State Chem.* 2020, 58, 100254. [CrossRef]
- 3. Kesavan, T.; Sundhar, A.S.R.; Dharaneshwar, S.; Prabu, N.; Manickam, S. N-Doped carbon nanosheets from biomass for ultra long-cycling and high energy density symmetric supercapacitors. *ECS J. Solid State Sci. Technol.* **2021**, *10*, 051004. [CrossRef]
- Cheng, Y.; Xie, Y.; Ma, Y.; Wang, M.; Zhang, Y.; Liu, Z.; Yan, S.; Ma, N.; Liu, M.; Yue, Y. Optimization of ion/electron channels enabled by multiscale MXene aerogel for integrated self-healable flexible energy storage and electronic skin system. *Nano Energy* 2023, 107, 108131. [CrossRef]
- 5. Geldasa, F.T.; Kebede, M.A.; Shura, M.W.; Hone, F.G. Identifying surface degradation, mechanical failure, and thermal instability phenomena of high energy density Ni-rich NCM cathode materials for lithium-ion batteries: A review. *RSC Adv.* **2022**, *12*, 5891–5909. [CrossRef] [PubMed]
- Maurel, A.; Russo, R.; Grugeon, S.; Panier, S.; Dupont, L. Environmentally friendly lithium-terephthalate/polylactic acid composite filament formulation for lithium-ion battery 3D-printing via fused deposition modeling. *ECS J. Solid State Sci. Technol.* 2021, 10, 037004. [CrossRef]
- Liu, Y.; Jiang, S.; Shao, Z. Intercalation pseudocapacitance in electrochemical energy storage: Recent advances in fundamental understanding and materials development. *Mater. Today Adv.* 2020, 7, 100072. [CrossRef]
- Zhang, F.; Zhang, T.; Yang, X.; Zhang, L.; Leng, K.; Huang, Y.; Chen, Y. A high-performance supercapacitor-battery hybrid energy storage device based on graphene-enhanced electrode materials with ultrahigh energy density. *Energy Environ. Sci.* 2013, 6, 1623–1632. [CrossRef]
- Liu, Y.; Zhang, D.; Shang, Y.; Liu, Y.; Zhang, J. Synthesis of nitrogen-doped graphene as highly effective cathode materials for Li-ion hybrid supercapacitors. J. Electrochem. Soc. 2015, 162, A2123. [CrossRef]
- Xu, J.; Li, Y.; Wang, L.; Cai, Q.; Li, Q.; Gao, B.; Zhang, X.; Huo, K.; Chu, P.K. High-energy lithium-ion hybrid supercapacitors composed of hierarchical urchin-like WO 3/C anodes and MOF-derived polyhedral hollow carbon cathodes. *Nanoscale* 2016, *8*, 16761–16768. [CrossRef]
- 11. Subramanian, V.; Luo, C.; Stephan, A.M.; Nahm, K.; Thomas, S.; Wei, B. Supercapacitors from activated carbon derived from banana fibers. *J. Phys. Chem. C* 2007, 111, 7527–7531. [CrossRef]
- 12. Tomboc, G.M.; Tesfaye Gadisa, B.; Jun, M.; Chaudhari, N.K.; Kim, H.; Lee, K. Carbon transition-metal oxide electrodes: Understanding the role of surface engineering for high energy density supercapacitors. *Chem. Asian J.* **2020**, *15*, 1628–1647. [CrossRef] [PubMed]
- 13. Zhang, S.; Pan, N. Supercapacitors performance evaluation. Adv. Energy Mater. 2015, 5, 1401401. [CrossRef]
- Hu, Z.; Sayed, S.; Jiang, T.; Zhu, X.; Lu, C.; Wang, G.; Sun, J.; Rashid, A.; Yan, C.; Zhang, L. Self-Assembled Binary Organic Granules with Multiple Lithium Uptake Mechanisms toward High-Energy Flexible Lithium-Ion Hybrid Supercapacitors. *Adv. Energy Mater.* 2018, *8*, 1802273. [CrossRef]
- Wang, H.; Qian, R.; Cheng, Y.; Wu, H.-H.; Wu, X.; Pan, K.; Zhang, Q. Micro/nanostructured TiNb<sub>2</sub>O<sub>7</sub>-related electrode materials for high-performance electrochemical energy storage: Recent advances and future prospects. *J. Mater. Chem. A* 2020, *8*, 18425–18463. [CrossRef]
- Mou, J.; Deng, Y.; Song, Z.; Zheng, Q.; Lam, K.H.; Lin, D. Excellent rate capability and cycling stability in Li<sup>+</sup>-conductive Li<sub>2</sub>SnO<sub>3</sub>-coated LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode materials for lithium-ion batteries. *Dalton Trans.* 2018, 47, 7020–7028. [CrossRef] [PubMed]
- 17. Zhang, Y.; Xie, H.; Jin, H.; Zhang, Q.; Li, Y.; Li, X.; Li, K.; Bao, C. Research Status of Spinel LiMn<sub>2</sub>O<sub>4</sub> Cathode Materials for Lithium Ion Batteries. *Proc. IOP Conf. Ser. Earth Environ. Sci.* **2020**, *603*, 012051. [CrossRef]

- 18. Xiang, M.; Zheng, J.; Li, S.; Hu, C.; Cui, J.; Zhang, Y.; Qi, Q.; Yue, F. Preparation of coated Li<sub>2</sub>TiO<sub>3</sub> and Li<sub>4</sub>SiO<sub>4</sub> pebbles by fluidized bed chemical vapor deposition for advanced tritium breeders. *Fusion Eng. Des.* **2021**, *165*, 112245. [CrossRef]
- 19. Hodeau, J.; Marezio, M.; Santoro, A.; Roth, R. Neutron profile refinement of the structures of Li<sub>2</sub>SnO<sub>3</sub> and Li<sub>2</sub>ZrO<sub>3</sub>. J. Solid State Chem. **1982**, 45, 170–179. [CrossRef]
- 20. Chen, J.-Z.; Hsu, C.-C.; Wang, C.; Liao, W.-Y.; Wu, C.-H.; Wu, T.-J.; Liu, H.-W.; Chang, H.; Lien, S.-T.; Li, H.-C. Rapid atmosphericpressure-plasma-jet processed porous materials for energy harvesting and storage devices. *Coatings* **2015**, *5*, 26–38. [CrossRef]
- 21. Lietz, A.M.; Johnsen, E.; Kushner, M.J. Plasma-induced flow instabilities in atmospheric pressure plasma jets. *Appl. Phys. Lett.* **2017**, *111*, 114101. [CrossRef]
- 22. Park, J.; Henins, I.; Herrmann, H.; Selwyn, G. Gas breakdown in an atmospheric pressure radio-frequency capacitive plasma source. *J. Appl. Phys.* 2001, *89*, 15–19. [CrossRef]
- 23. Kostov, K.G.; Nishime, T.M.C.; Castro, A.H.R.; Toth, A.; Hein, L.R.D.O. Surface modification of polymeric materials by cold atmospheric plasma jet. *Appl. Surf. Sci.* 2014, 314, 367–375. [CrossRef]
- 24. Liao, W.-Y.; Chang, H.; Yang, Y.-J.; Hsu, C.-C.; Cheng, I.-C.; Chen, J.-Z. Oxygen-deficient indium tin oxide thin films annealed by atmospheric pressure plasma jets with/without air-quenching. *Appl. Surf. Sci.* **2014**, 292, 213–218. [CrossRef]
- 25. Suenaga, Y.; Takamatsu, T.; Aizawa, T.; Moriya, S.; Matsumura, Y.; Iwasawa, A.; Okino, A. Influence of controlling plasma gas species and temperature on reactive species and bactericidal effect of the plasma. *Appl. Sci.* **2021**, *11*, 11674. [CrossRef]
- Chang, J.-H.; Lin, M.-F.; Kuo, Y.-L.; Yang, C.-R.; Chen, J.-Z. Flexible rGO-SnO2 supercapacitors converted from pastes containing SnCl2 liquid precursor using atmospheric-pressure plasma jet. *Ceram. Int.* 2021, 47, 1651–1659. [CrossRef]
- 27. Gorduk, O.; Gorduk, S.; Sahin, Y. Fabrication of tetra-substituted copper (II) phthalocyanine-graphene modified pencil graphite electrode for amperometric detection of hydrogen peroxide. *ECS J. Solid State Sci. Technol.* **2020**, *9*, 061003. [CrossRef]
- Chiang, M.-H.; Liao, K.-C.; Lin, I.-M.; Lu, C.-C.; Huang, H.-Y.; Kuo, C.-L.; Wu, J.-S. Modification of hydrophilic property of polypropylene films by a parallel-plate nitrogen-based dielectric barrier discharge jet. *IEEE Trans. Plasma Sci.* 2010, 38, 1489–1498. [CrossRef]
- Kull, K.R.; Steen, M.L.; Fisher, E.R. Surface modification with nitrogen-containing plasmas to produce hydrophilic, low-fouling membranes. J. Membr. Sci. 2005, 246, 203–215. [CrossRef]
- 30. Pieta, P.; Obraztsov, I.; D'Souza, F.; Kutner, W. Composites of conducting polymers and various carbon nanostructures for electrochemical supercapacitors. *ECS J. Solid State Sci. Technol.* **2013**, *2*, M3120. [CrossRef]
- Kuok, F.-H.; Liao, C.-Y.; Chen, C.-W.; Hao, Y.-C.; Yu, S.; Chen, J.-Z. Screen-printed SnO2/CNT quasi-solid-state gel-electrolyte supercapacitor. *Mater. Res. Express* 2017, 4, 115501. [CrossRef]
- 32. Secor, E.B.; Gao, T.Z.; Islam, A.E.; Rao, R.; Wallace, S.G.; Zhu, J.; Putz, K.W.; Maruyama, B.; Hersam, M.C. Enhanced conductivity, adhesion, and environmental stability of printed graphene inks with nitrocellulose. *Chem. Mater.* 2017, *29*, 2332–2340. [CrossRef]
- Wang, Q.; Wu, M.; Meng, S.; Zang, X.; Dai, Z.; Si, W.; Huang, W.; Dong, X. Hydrazine sensor based on Co<sub>3</sub>O<sub>4</sub>/rGO/carbon cloth electrochemical electrode. *Adv. Mater. Interfaces* 2016, *3*, 1500691. [CrossRef]
- Wang, Q.; Huang, Y.; Zhao, Y.; Zhang, W.; Wang, Y. Preparation of Li2SnO3 and its application in lithium-ion batteries. *Surf. Interface Anal.* 2013, 45, 1297–1303. [CrossRef]
- Yue, L.; Zhang, Y.; Sun, W.; Luo, X.; Lian, J.; Li, Z.; Jiang, Y.; Zhang, W. Synthesis of a novel (NH<sub>4</sub>)<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>Sn/TiO<sub>2</sub> heterostructure for efficient photocatalytic degradation and removal of water pollutants. *Mater. Lett.* 2019, 237, 137–140. [CrossRef]
- 36. Cheng, S.; He, Y.; Chen, G.; Cho, E.-C.; Conibeer, G. Influence of EDTA concentration on the structure and properties of SnS films prepared by electro-deposition. *Surf. Coat. Technol.* **2008**, 202, 6070–6074. [CrossRef]
- Zhang, X.; Dong, P.; Lee, J.-I.; Gray, J.T.; Cha, Y.-H.; Ha, S.; Song, M.-K. Enhanced cycling performance of rechargeable Li–O<sub>2</sub> batteries via LiOH formation and decomposition using high-performance MOF-74@ CNTs hybrid catalysts. *Energy Storage Mater.* 2019, *17*, 167–177. [CrossRef]
- Rani, B.; Nayak, A.K.; Sahu, N.K. Electrochemical supercapacitor application of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles decorated over graphitic carbon nitride. *Diam. Relat. Mater.* 2021, 120, 108671. [CrossRef]
- 39. Kour, S.; Tanwar, S.; Sharma, A. A review on challenges to remedies of MnO<sub>2</sub> based transition-metal oxide, hydroxide, and layered double hydroxide composites for supercapacitor applications. *Mater. Today Commun.* **2022**, *32*, 104033. [CrossRef]
- 40. Liu, C.; Hung, C.-W.; Cheng, I.-C.; Hsu, C.-C.; Cheng, I.-C.; Chen, J.-Z. Dielectric barrier discharge plasma jet (DBDjet) processed reduced graphene oxide/polypyrrole/chitosan nanocomposite supercapacitors. *Polymers* 2021, *13*, 3585. [CrossRef]
- 41. Gunasekaran, S.S.; Veeralingam, S.; Badhulika, S. "One for two" strategy of fully integrated textile based supercapacitor powering an ultra-sensitive pressure sensor for wearable applications. *J. Energy Storage* **2022**, *48*, 103994. [CrossRef]

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