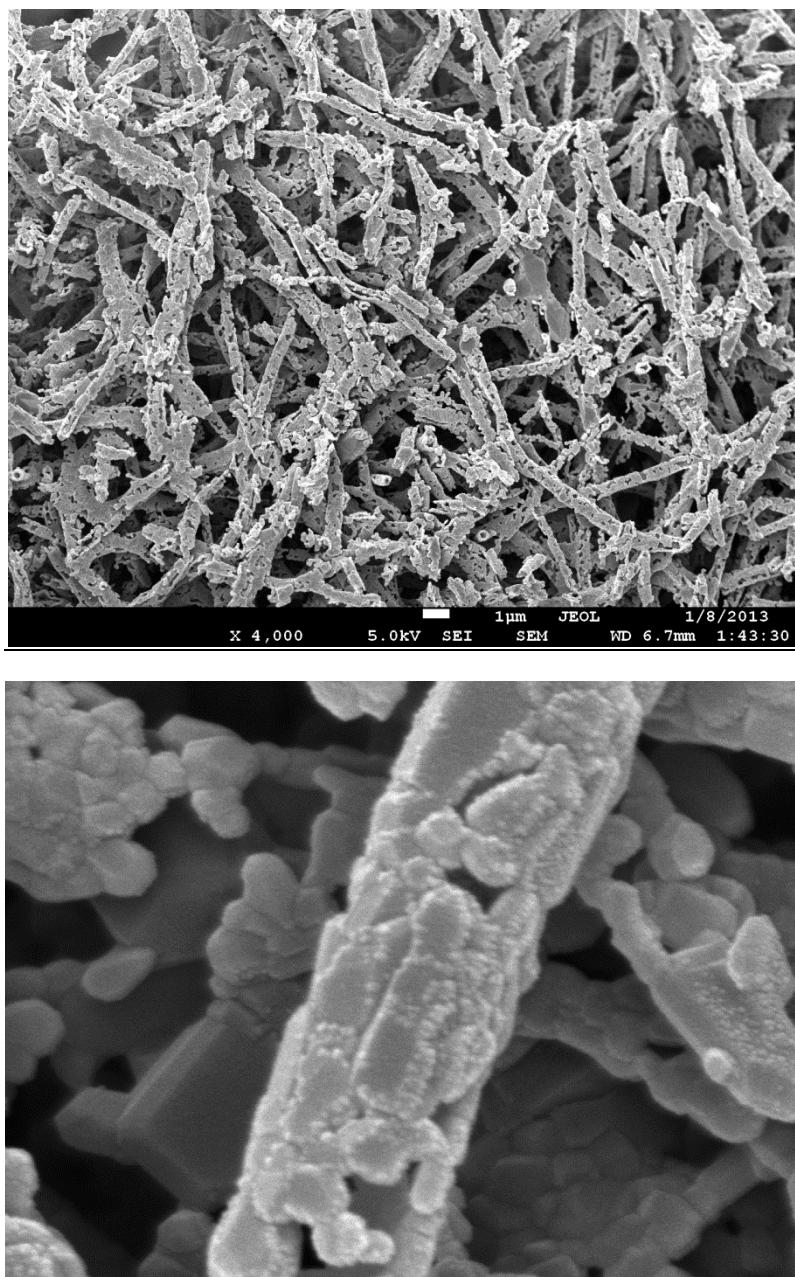


## Supplementary information

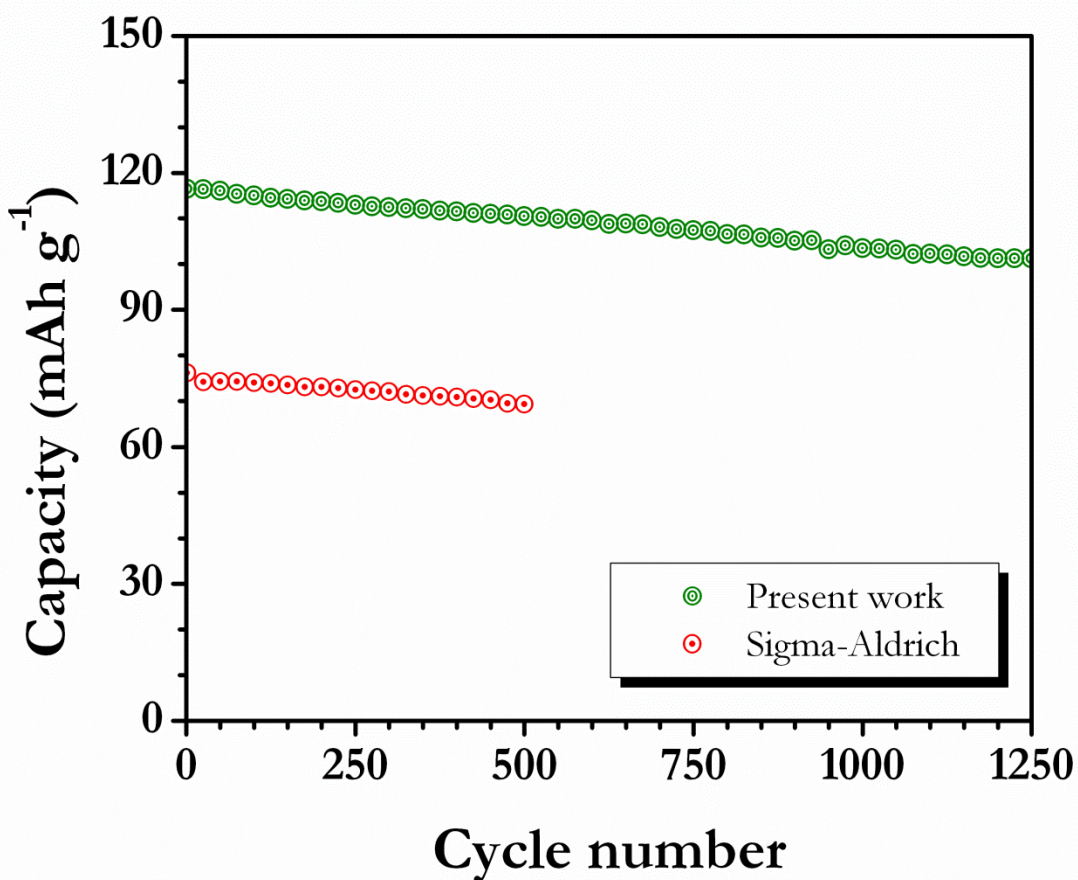
### Experimental Section

One dimensional electrospun  $\text{LiMn}_2\text{O}_4$  hollow nanofibers were synthesized by simple electrospinning technique. In the typical synthesis procedure, manganese acetate dihydrate  $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ , lithium nitrate and Ethanol (HPLC grade), polyvinylpyrrolidone (PVP,  $M_w$ : 130000) and acetic acid (99.7%) were purchased from Aldrich and used without any further purification. In a typical synthesis, homogeneous sol-gel solution was prepared by mixing 1.5 g of PVP in 15 ml ethanol under constant stirring for an hour. Then, 0.3 g of lithium nitrate and 2.33 g of manganese acetate dehydrate was added simultaneously in the homogeneous polymer solution and stirred again. Finally, 1 ml of acetic acid was added to the solution under vigorous stirring for  $\sim 12$  h. The prepared sol-gel solution was then transferred into a 5 ml syringe (dia. of 11.9 mm) with  $18\frac{1}{2}$  G stainless steel needle which has a diameter of 0.084 cm. The experiment has been carried out in a controlled electrospinning setup (ELECTROSPUNRA, Microtools Pvt. limited, and Singapore). The humidity level of the synthesis electrospinning chamber was maintained at about 35% for the whole experimental process. The distance between needle and static collector (aluminum foil) was maintained at 16 cm with an applied ac voltage of 22 kV and at a flow rate of  $0.7 \text{ ml h}^{-1}$  using a syringe pump (KDS 200). Finally, the prepared composite fibers were collected and immediately preheated at  $500 \text{ }^\circ\text{C}$  for 1 h and further sintered at  $800 \text{ }^\circ\text{C}$ , with a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$  for 5 h under air atmosphere to yield  $\text{LiMn}_2\text{O}_4$  hollow nanofibers.

Powder X-ray diffraction (XRD) measurements were conducted using Bruker AXS, D8 Advance instruments equipped with Cu  $K\alpha$  radiation. Rietveld refinement also carried out for the observed reflections using Topas V3 software. Surface morphology and internal structure of the hollow nanofibers were analyzed using field emission scanning electron microscope (FE-SEM, JEOL JFM-6340F) and transmission electron microscope (TEM, JEOL 2100F), respectively. Electrochemical studies were conducted in standard two electrode CR 2016 coin-cell configurations. Composite cathodes were prepared by mixing with accurately weighed 10 mg of active material ( $\text{LiMn}_2\text{O}_4$ ), 1.5 mg of super P, and 1.5 mg of conductive binder (Teflonized acetylene black, TAB-2) using ethanol. Then the mixture was pressed over a  $200 \text{ mm}^2$  stainless steel mesh (Goodfellow, UK), which served as a current collector during electrochemical studies and dried at  $60 \text{ }^\circ\text{C}$  for overnight before conducting coin-cell assembly in Ar filled glove box (MBraun, Germany). Microporous glass fibers (Whatman, Cat. No. 1825-047, UK) were used to physically separate the test electrodes in coin-cell assembly and filled with 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/di-methyl carbonate (DMC) (Selectipure SP30, Merck KGaA, Germany) as electrolyte solution. Cyclic voltammograms (CV) were recorded using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat in two electrode configurations at slow scan rate of  $0.1 \text{ mV s}^{-1}$  between 3.5-4.3 V vs. Li. For the CV measurements, metallic lithium acts as both counter and reference electrode. Galvanostatic studies were performed at constant current mode using Arbin 2000 battery tester in ambient ( $25 \text{ }^\circ\text{C}$ ) and elevated temperature ( $55 \text{ }^\circ\text{C}$ ) conditions.

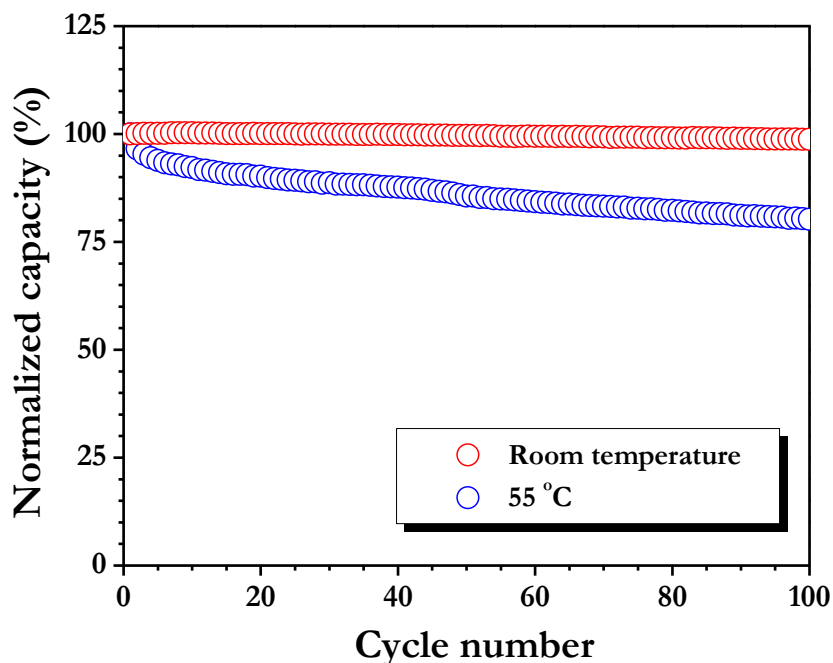


**Figure S1:** FE-SEM pictures of electrospun  $\text{LiMn}_2\text{O}_4$  hollow nanofibers



**Figure S2** Plot of discharge capacity vs. cycle number for  $\text{LiMn}_2\text{O}_4$  hollow nanofibers in half-cell assembly tested between 3.5-4.3 V vs. Li at current density of  $150 \text{ mA g}^{-1}$  (Data points were collected after every 25 cycles).

For commercial  $\text{LiMn}_2\text{O}_4$  cathodes, the electrodes are formulated with accurately weighed 10 mg of active material, 2 mg of super P, and 2 mg of TAB-2 over  $200 \text{ mm}^2$  stainless steel mesh.

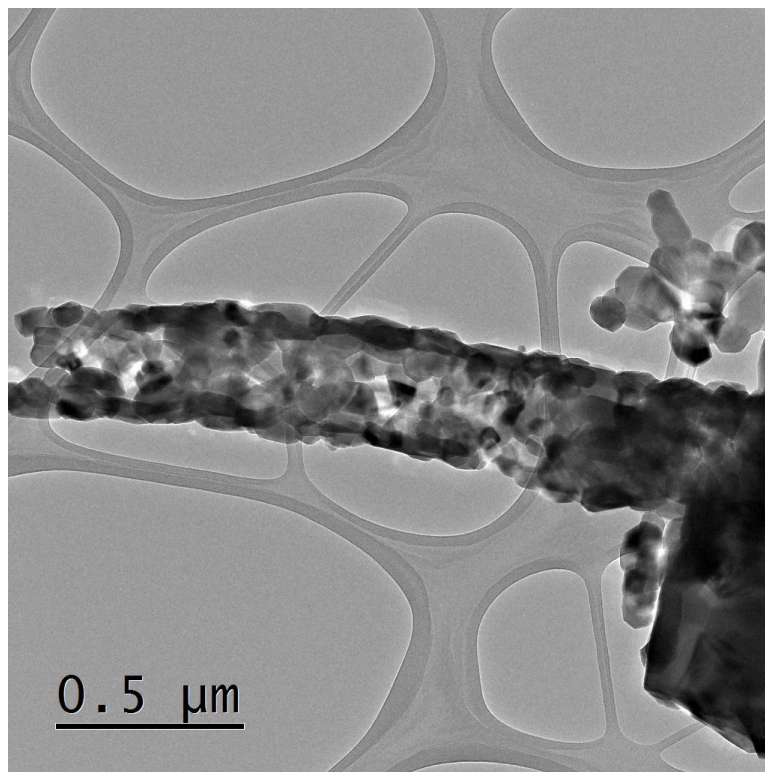


**Figure S3** Plot of discharge capacity *vs.* cycle number for LiMn<sub>2</sub>O<sub>4</sub> hollow nanofibers in half-cell assembly at current rate of 150 mA g<sup>-1</sup> between 3.5-4.3 V *vs.* Li in ambient and elevated temperature conditions.

Elevated temperature (55 °C) performance is warranted for HEV and EV applications while utilizing such spinel LiMn<sub>2</sub>O<sub>4</sub> as cathodes. In this line, a duplicate cell has been fabricated and tested between 3.5-4.3 V *vs.* Li at high current rate of 150 mA g<sup>-1</sup> and shown in figure S3. At high temperature conditions test cell delivered the reversible capacity ~122 mAh g<sup>-1</sup> which is normalized to 100% for comparison with room temperature performance. Apparent to note that after 100 cycles the test cell rendered ~98.7 and 80.2% of capacity retention for ambient and elevated temperature conditions, respectively. This is one of the best results, reported for LiMn<sub>2</sub>O<sub>4</sub> based materials in elevated temperature conditions. Since, at high temperature conditions the reactivity between electrolyte and electrode materials are found severe. As a result Mn dissolution rate will be higher. In order to prevent such dissolution, surface modification will be employed<sup>1,2</sup>. Here, without any surface modification, our electrospun hollow LiMn<sub>2</sub>O<sub>4</sub> nanofibers delivered exceptional performance compared to the works presented literature<sup>2,3</sup>. This behavior is mainly attributed to the presence of one dimensional hollow structures prepared by electrospinning which facilitates faster diffusion of Li-ions especially at high current rates. Excellent stoichiometry and robust nature of such hollow structures cannot be ruled out for such exceptional performance (Figure S4).

1. J. Cho, T.-J. Kim, Y. J. Kim and B. Park, *Chemical Communications*, 2001, **0**, 1074-1075.
2. C. Li, H. P. Zhang, L. J. Fu, H. Liu, Y. P. Wu, E. Rahm, R. Holze and H. Q. Wu, *Electrochim. Acta*, 2006, **51**, 3872-3883.
3. S.-T. Myung, K. Amine and Y.-K. Sun, *J. Mater. Chem.*, 2010, **20**, 7074-7095.





**Figure S4:** TEM pictures of electrospun  $\text{LiMn}_2\text{O}_4$  hollow nanofibers after 1250 cycles and still retains the fibrous morphology. This clearly indicates excellent robust nature of such fibers prepared by electrospinning.