Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

High performance 3D Printed Faradaic Supercapacitor Using Hybrid Nanocomposites of Reduced Graphene oxide/Mn_xO_y-based Electrodes

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Parameter	Value
Pattern width	25mm
Pattern length	32mm
Line length	17mm
Line width	1.2mm
Line-to-line space	2mm

Figure S 1. *Interdigitated fillet printing pattern of the silver current collector, active layers, and printed design dimensions. The shape and size of the printed pattern can be customized and will be studied in the future works. In this study, fillet pattern was developed to handle the convenience, printer compatibility, and reproducibility while improving the strength of printed design by avoiding right angle and also keeping consistent printing.*

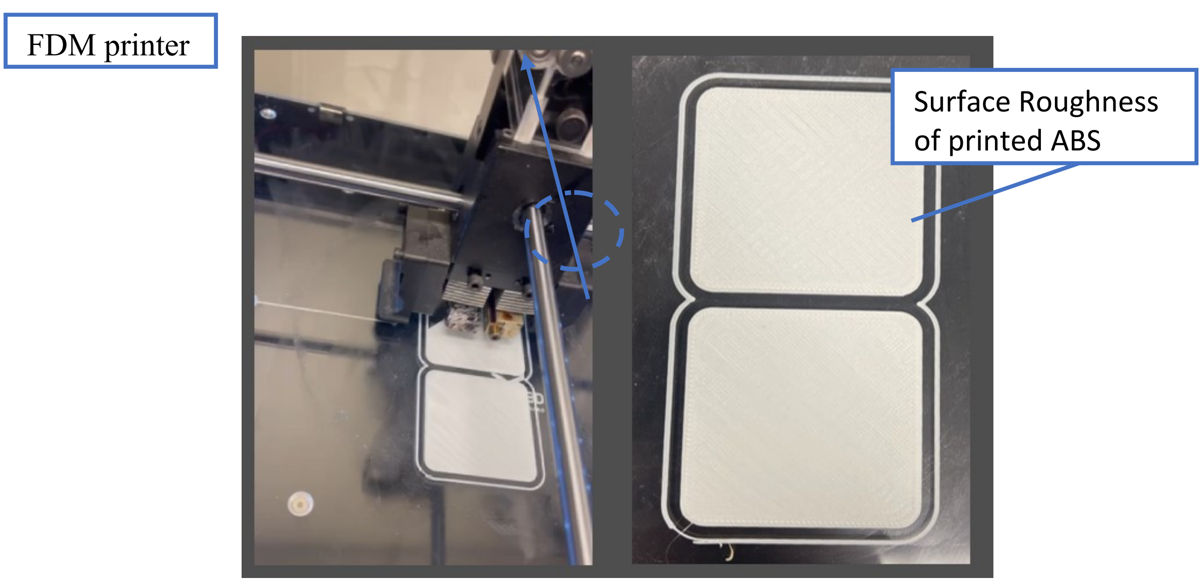

Figure S 2. The filament printed ABS substrate fabricated by an FDM printer. The role of the substrate is to support all other functional layers including current-collector, active, and Gel Polymer layers. As you see in this figure, the surface roughness of ABS printed substrate was maintained to help with the ink adhesion.

Examples of substrates failures:

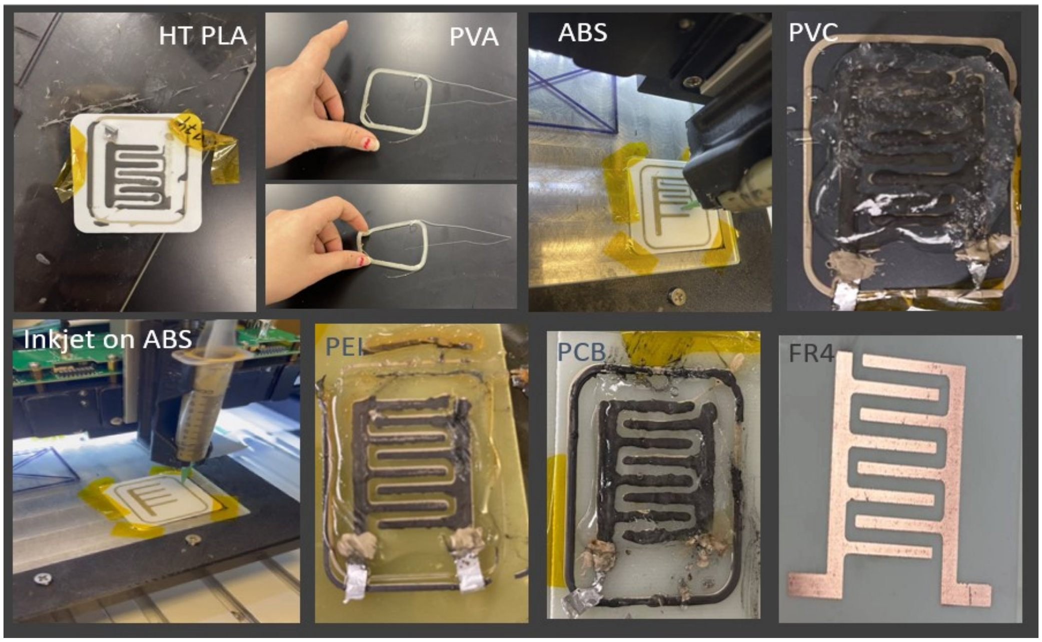

Figure S 3. Various prefabricated substrates were investigated in this study (such as, Polyvinyl alcohol (PVA), High Temperature Polylactide (HTPLA), Polyvinyl chloride (PVC), Polyetherimide (PEI), etc.). As illustrated in this figure, the printing failures on the substrate were the main reason for using our custom 3D printed ABS substrate instead of these prefabricated commercially existing substrates to fabricate an all-printed SC design. The printed ABS substrate could support the current collector, active and gel polymer layer and it was perfectly compatible with the annealing temperature required for each layer. Therefore, no thermal degradation (cracking, chipping, and breaking) was observed. ABS did not show any adhesion failure and it was also compatible with the solvent we used to prepare the gel polymer layer.

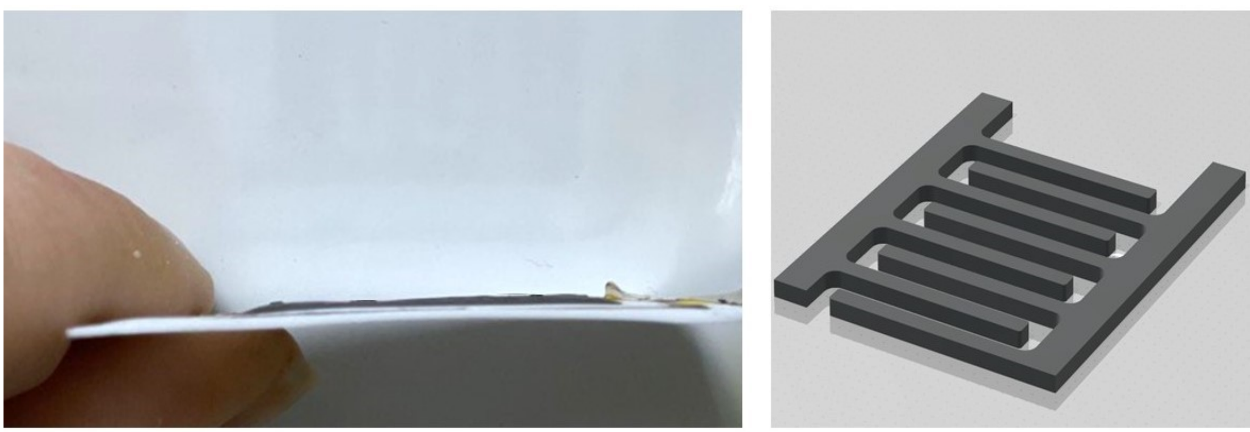

Figure S 4. Design pattern created with the solid work with 1mm height of each layer.

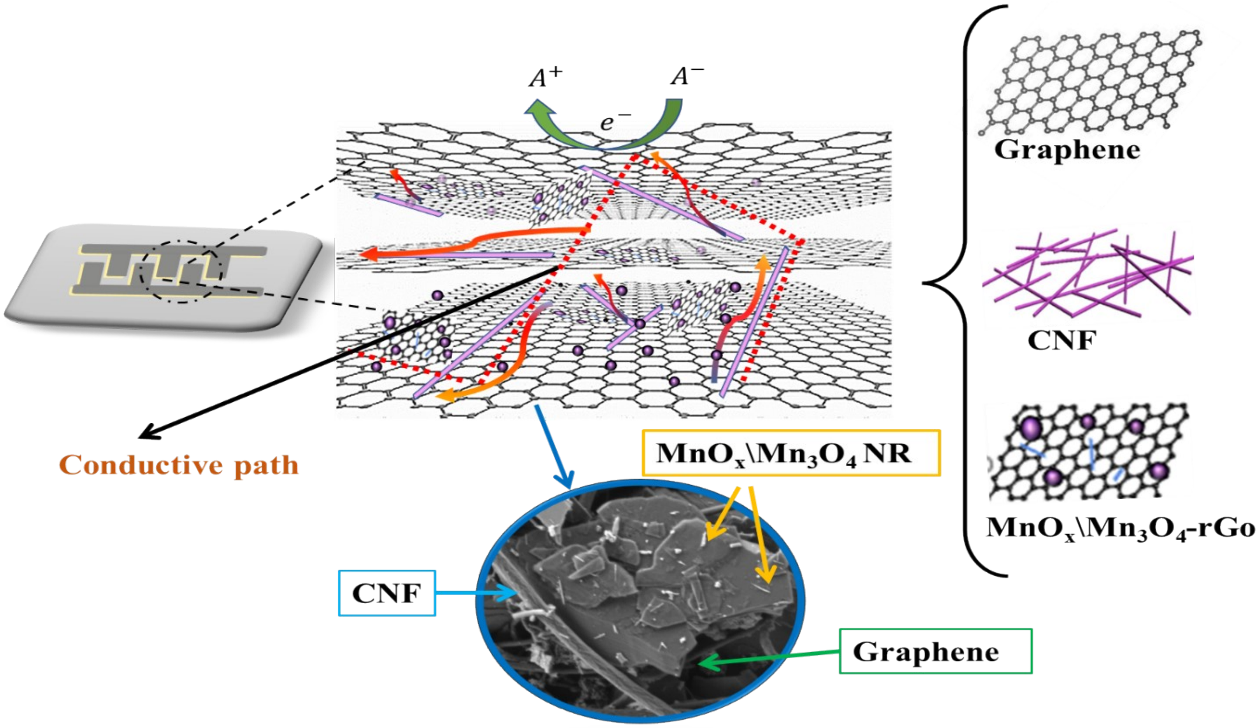

Figure S 5. Schematic illustration of the percolated conductive network of CNFs, MnO_x/Mn_3O_4 -rGo on graphene nanosheets.

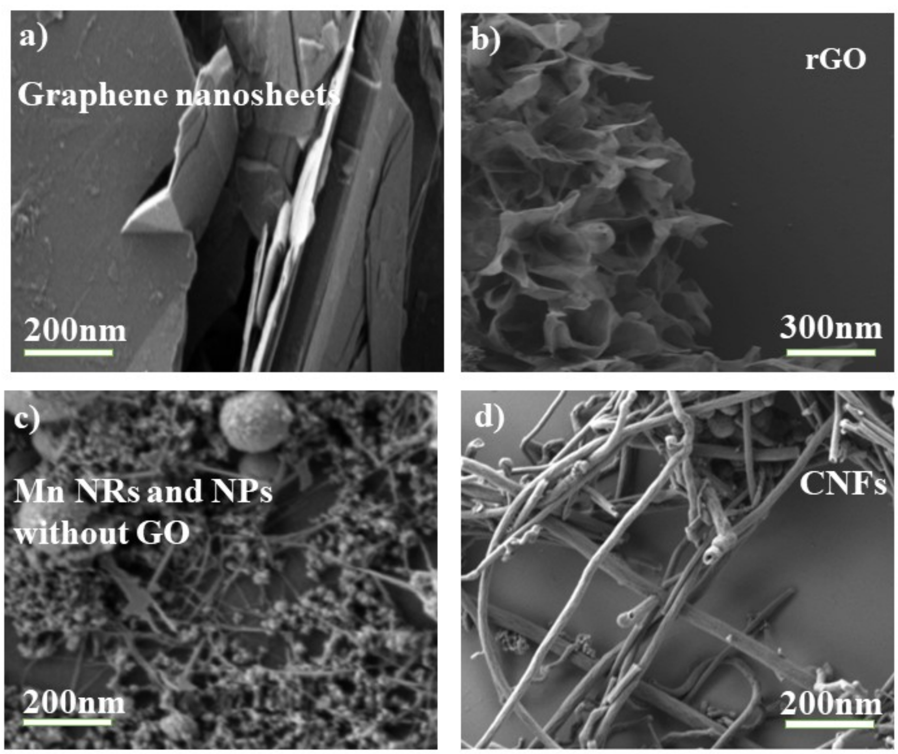

Figure S 6. SEM micrographs of all active-printed electrode constituents in their respective pristine phases: (a) graphene nanosheets, (b) reduced graphene-oxide (rGO) (c) Mn_xO_y nano-architectures obtained from the laser ablatio of Mn target during 8 min, and (d) Carbon nanofibers (CNTs)

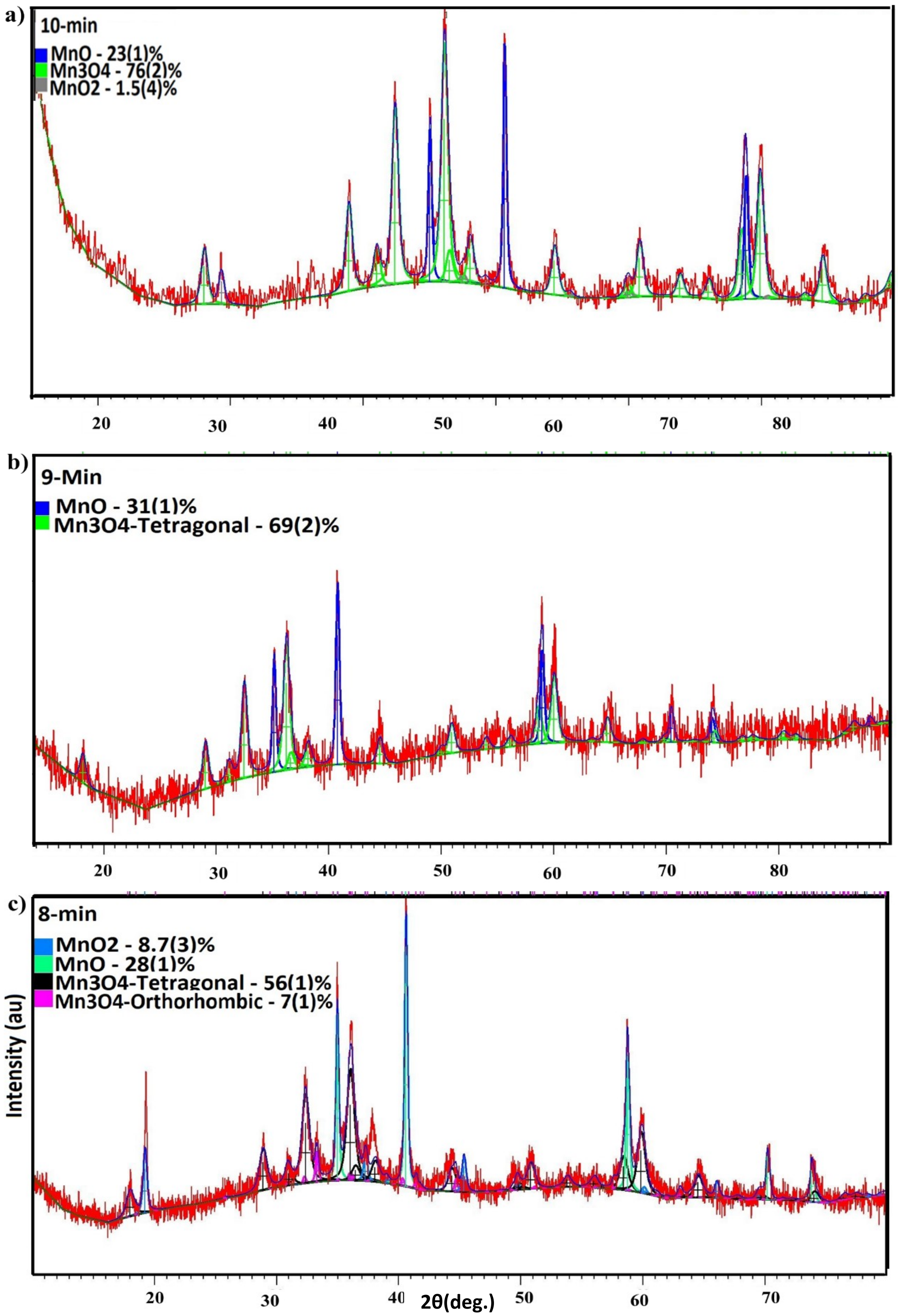

Figure S 7. XRD peak patterns for samples prepared at 8- 9- and 10 mins ablation time. There patterns indicate that various manganese oxide structures could be detected in the nanocomposites formed during the LASiS-induced synthesis of the HNCs.

XRD patterns of samples prepared under 9- and 10- mins of ablation times indicate negligible presence of MnO_2 crystal structures in the HNCs structure while its mass ratio for the sample prepared under 8- mins ablation time is around 9%.

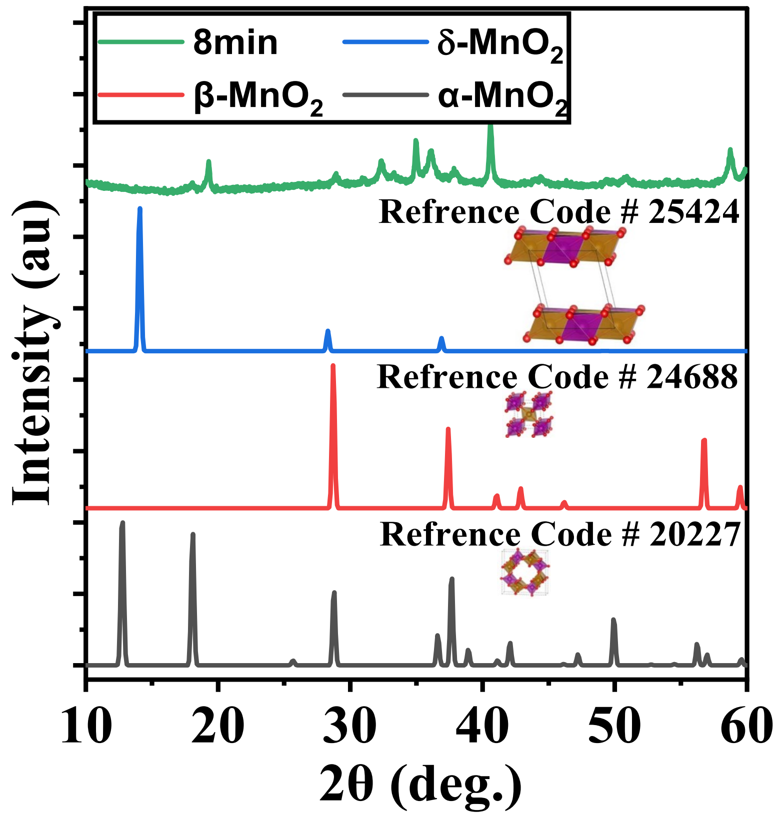

Figure S 8. XRD pattern of the Laser derived MnO_x /Mn_3O_4-rGO HNCs prepared under 8 minutes ablation time and comparison with standard XRD pattern of α-, β- & δ-MnO_2. There is a distinct peak for α-MnO_2 around 2θ=18 and 2θ=39 (deg).

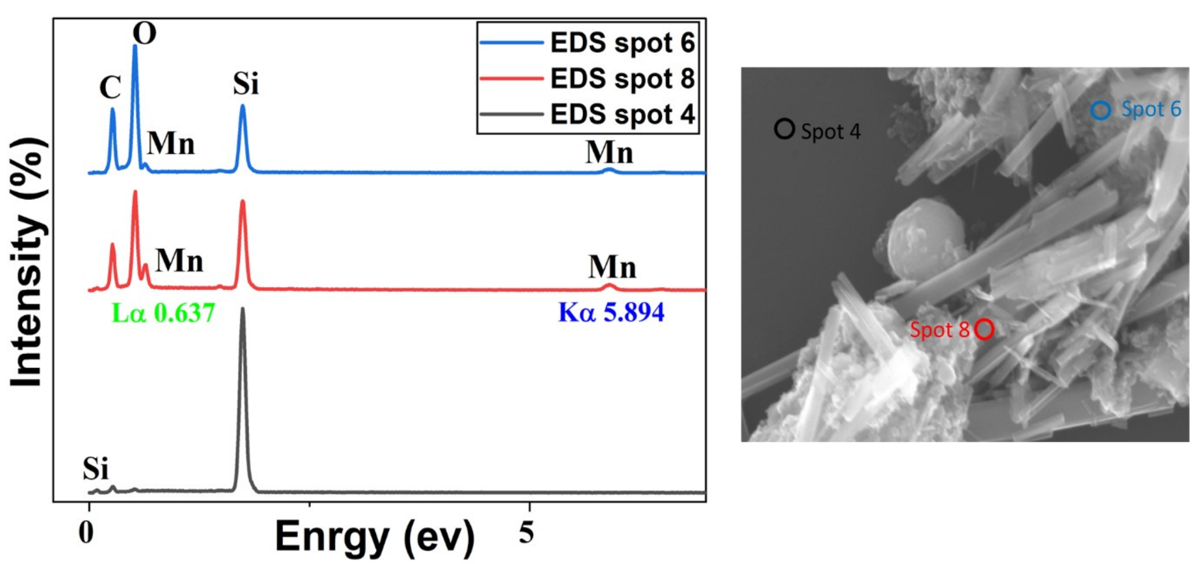

Figure S 9. EDS spectra of MnO_x/Mn_3O_4-rGO prepared under 8 min ablation on a Si wafer confirming presence of Mn, C, and O components on the Si by EDS and STEM measurements

Proposed sequence of lithiation reactions and surface redox reactions in the printed-supercapacitor cell:

According to Choi *et al.*, for pseudocapacitive materials, there are two main mechanisms of charge storage: surface redox pseudocapacitance and intercalation pseudocapacitance[1].

In general case, the surface redox transformation and ion intercalation into metal-oxide electrode can be written as[2]:

$M_xO_y + \delta Ct^+ + \delta e^- \leftrightarrow M_xO_yCt_\delta$

Therefore, to modify surface adsorption of electrolyte cations (Li^+) on the Mn oxide for the 3-electode system using Ag/AgCl as a reference electrode, we suggest the following reactions[3.4]:

1. **MnO**

$$MnO + xLi^+ + xe^- \leftrightarrow MnOLi_x (I)$$

2. **MnO_2**

$$MnO_2 + xLi^+ + xe^- \leftrightarrow MnOOLi_x\ (II)$$

3. **Mn_3O_4**

$Mn_3O_4 + xLi^+ + xe^- \leftrightarrow Mn_3O_4Li_x\ (III)$

Also, the sequence of proposed reversible faradaic reactions occurring during the discharging process at the interface between the redox-active electrode and gel polymer electrolyte for the various manganese-oxide phases is detailly outlined below[5]:

1. **MnO**

$MnO + 2Li^+ + 2e^- \leftrightarrow Mn + Li_2O\ (I)$

2. **MnO_2**

$MnO_2 + Li^+ + e^- \leftrightarrow LiMnO_2\ (II)$

$LiMnO_2 + Li^+ + e^- \leftrightarrow Li_2MnO_2\ (III)$

$Li_2MnO_2 + 2Li^+ + e^- \leftrightarrow Mn + 2Li_2O\ (IV)$

3. Mn_3O_4

$Mn_3O_4 + Li^+ + e^- \leftrightarrow LiMn_3O_4\ (V)$

$LiMn_3O_4 + Li^+ + e^- \leftrightarrow 3\ MnO + Li_2O\ (VI)$

$MnO +\ 2Li^+ + 2e^- \leftrightarrow Mn + Li_2O\ (I)$

Table 1. Power and Energy density of printed SCs.

Sample	Specific current of GCD [A/g]	Power Density [W/kg]	Energy density [Wh/kg]
Commercial Ink	1	906	17.1
Synthesized Ink	1	1002	32.8

References:

1. Choi, C., Ashby, D. S., Butts, D. M., DeBlock, R. H., Wei, Q., Lau, J., & Dunn, B., Achieving high energy density and high-power density with pseudocapacitive materials. *Nature Reviews Materials*, 2020, *5*(1), 5-19.
2. Pronkin, S. N., Shokina, N. Y., & Pham-Huu, C., Redox Transitions in Pseudocapacitor Materials: Criteria and Ruling Factors, 2022.
3. K. Kordesch, W. Taucher-Mautner, Chemistry, Electrochemistry, and Electrochemical Applications / Manganese, Editor(s): Jürgen Garche, Encyclopedia of Electrochemical Power Sources, *Elsevier*, 2009, 784-795, ISBN 9780444527455, https://doi.org/10.1016/B978-044452745-5.00838-8.
4. W. Wei, X. Cui, W. Chen, D.G. Ivey, Manganese Oxide-based Materials as Electrochemical Supercapacitor Electrodes. *Chemical Society Reviews*, 2011, 40(3), 1697-1721.
5. Fang, X., Lu, X., Guo, X., Mao, Y., Hu, Y. S., Wang, J., ... & Chen, L., Electrode reactions of manganese oxides for secondary lithium batteries. *Electrochemistry Communications*, 2010, *12*(11), 1520-1523.