Supporting Information

Electro-insertion of Mn^{2+} ions into $V_2O_5.nH_2O$ on MWCNTs Coated Carbon Felt for Binder-free Na^+ Ion Battery Electrodes

R. Parmar[1,2], D.B.de Freitas Neto[2], E. Y. Matsubara[2], R.Gunnella[1], J.M.Rosolen[2]

[1] *Physics Division, School of Science and Technology, University of Camerino, Via Madonna delle Carceri, 9, 62032 Camerino (MC), Italy and*

[2] *Department of Chemistry, FFCLRP, University of Sào Paulo,14040-930 Ribeirão Preto-SP, Brazil*

I. SAMPLES PREPARATION

The electro-deposited carbon felt substrate is shown in Fig.1. The electrodeposition process of samples S1, S3, S5 (on felt) and S2, S4, S6 (on MWCNT/felt) are shown in Fig.2. After every electrodeposition experiment, the samples were dried and measure the weight of active material. For the $Mn_xV_2O_5$ samples preparation, first we deposit the $V_2O_5.nH_2O$ on felt or MWCNT/felt then dry at 80 °C temperature measure the weight of electro-deposited mass and then electro-deposited the MnO_2 on the $V_2O_5.nH_2O$/felt or MWCNT/felt sample. After MnO_2 dry for overnight and measure the weight gain. The mass of electro-deposited active material are reported in mg in the table below Tab.I for the felt, MWCNTs and metal oxides (MnO_2, V_2O_5), from S1 to S6 respectively.

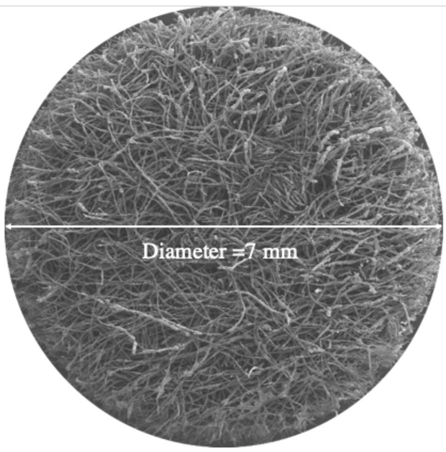

FIG. 1: The electro-deposited carbon felt substrate picture.

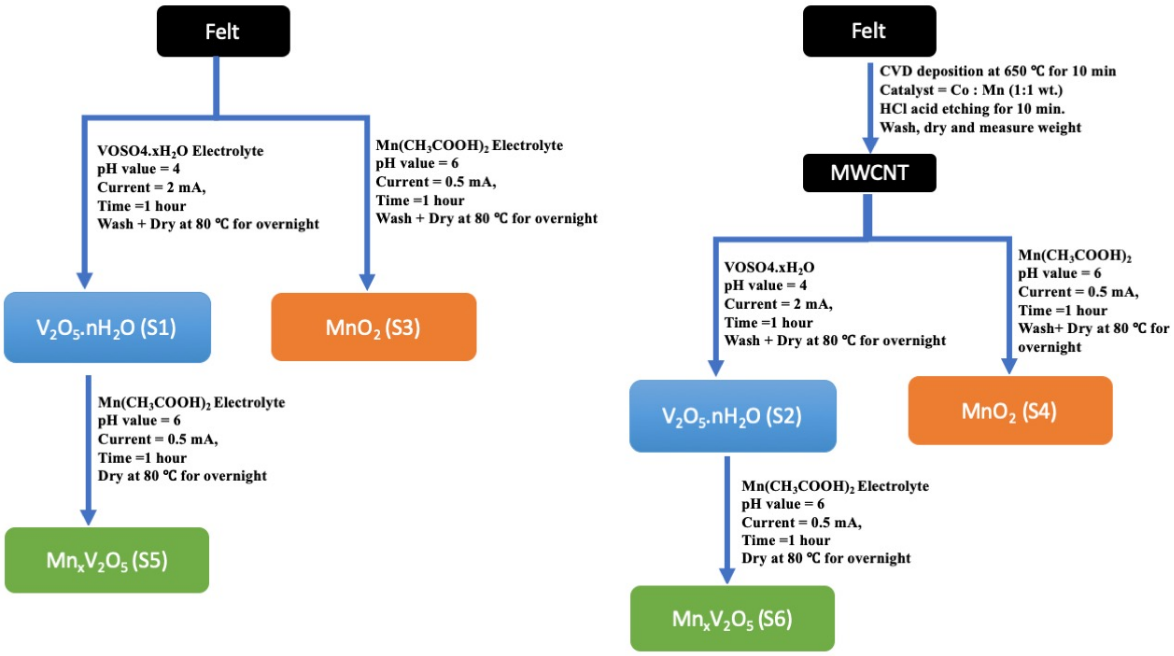

FIG. 2: The flow chart of electrodeposition process of samples on felt and MWCNT/felt substrates.

TABLE I: The mass in mg, for felt substrate, CVD deposited MWCNTs, electrodeposited V_2O_5 and MnO_2 respectively

Samples	**felt substrate (mg)**	**MWCNTs**	**V_2O_5**	**MnO_2**
S1 (V_2O_5.nH_2O/felt)	15.88	-	2.47	-
S2 (V_2O_5.nH_2O/MWCNTs/felt)	16.06	1.55	0.89	-
S3 (MnO_2/felt)	15.11	-	-	1.01
S4 (MnO_2/MWCNT/felt)	17.11	3.98	-	1.47
S5 ($Mn_xV_2O_5$/felt)	15.68	-	1.97	0.95
S6 ($Mn_xV_2O_5$/MWCNT/felt)	15.05	3.05	0.93	0.81

II. SCANNING ELECTRON MICROSCOPY

The low magnification images by scanning electron microscopy (SEM) of samples S1, S2, S3, S4, S5 and S6 respectively, show the material coating on carbon fibres and MWCNTs/carbon fibres. The purpose of these low magnified image to show the material coating on the carbon fibre (felt) and MWCNT coated felt substrates for $V_2O_5.nH_2O$, MnO_2 and $Mn_xV_2O_5$. The sample S6 ($Mn_xV_2O_5$/MWCNTs/felt) shows also platelets (Pts) like morphology, Fig.3-inset image. These nano-platelets have mostly manganese on their surface which were confirmed by energy dispersive x-ray spectrometry (EDXS) analysis.

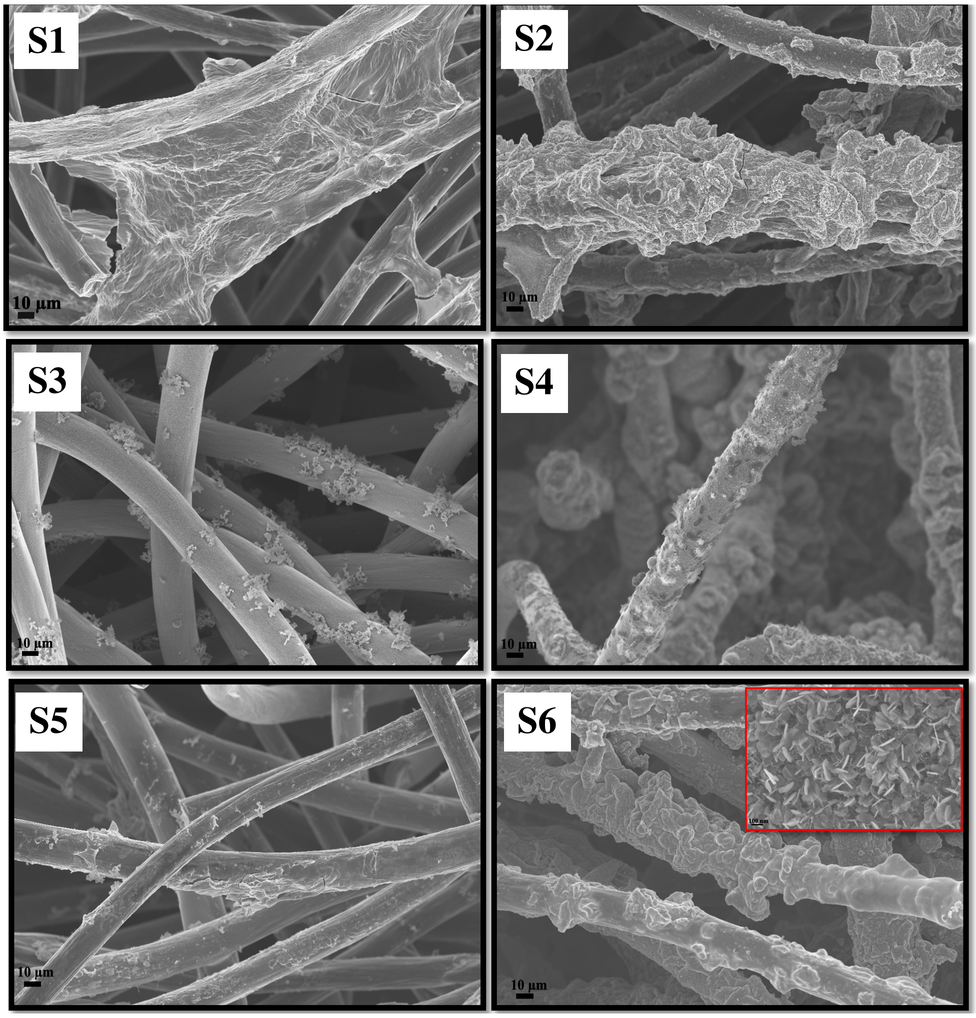

FIG. 3: The low magnification SEM images of samples: S1 ($V_2O_5.nH_2O$/felt), S2 ($V_2O_5.nH_2O$/MWCNTs/felt), S3 (MnO_2/felt), S4 (MnO_2/MWCNTs/felt), S5 ($Mn_xV_2O_5$/felt) and S6($Mn_xV_2O_5$/MWCNTs/felt) respectively.

In the Fig.4, there electro-deposited $V_2O_5.nH_2O$ on felt and MWCNT/felt are shown along with the uncovered bare felt and MWCNT/felt fibre. From the Fig.4-f, we can see the electro-deposited $V_2O_5.nH_2O$ are filling up the space or voids between the MWCNT network. This is the reason the behind the high material growth on MWCNT/felt (Fig.4-f) than felt substrate shown in Fig.4-d.

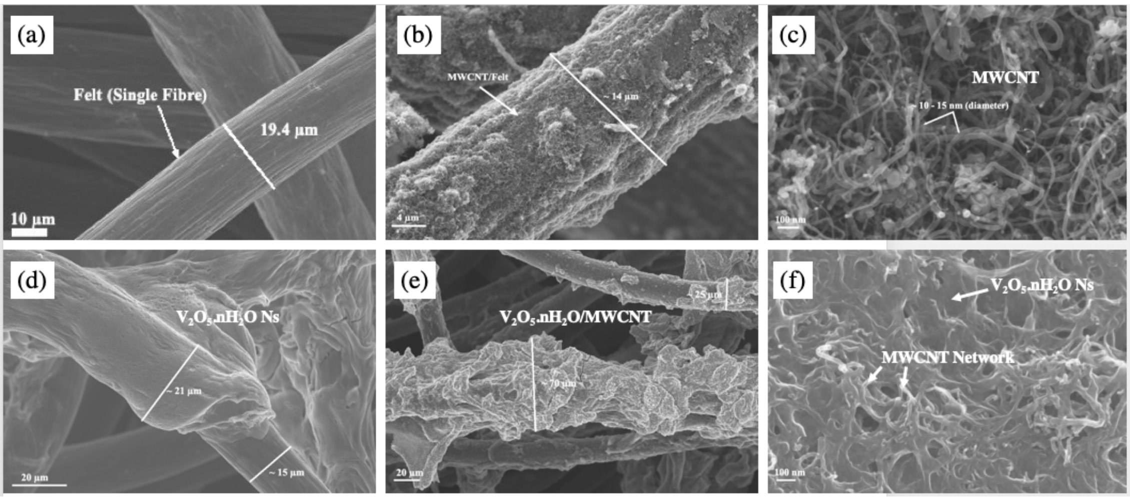

FIG. 4: The SEM images, uncovered carbon fibre (felt)- (a), MWCNT on felt fibre -(b), the hight magnification MWCNT image -(c), electro-deposited V_2O_5.nH_2O on felt -(d), electro-deposited V_2O_5.nH_2O on MWCNT/felt (e) and high magnified image of electro-deposited V_2O_5.nH_2O on MWCNT network on felt (f).

The dimensions of V_2O_5, MnO_2 and $Mn_xV_2O_5$ nanostructures (massive nanorods, nanoflakes or platelets, and MWCNTs) are calculated using high magnification SEM analysis. MWCNTs samples captured the atomic composition % of Cl and Co from acid etching and catalyst.

TABLE II: Measurements of nanostructures by high magnification SEM

Samples	**parameter**	nm
$V_2O_5.nH_2O$	coating thickness	~7 μm (S1)
$V_2O_5.nH_2O$/MWCNT	coating thickness	~ 10 to 30 μ (S2)
MWCNTs	diameter	~15 to 35 nm (S2)
MnO_2	coating thickness	~ 3 μm thick (S3)
MnO_2	nanorods width	~ 100 to 150 nm (S3)
MnO_2/MWCNT	coating thickness	~ 5 to 10 μm (S4)
$Mn_xV_2O_5$	coating thickness	~ 1 to 5 μm (S5)
MnxOy (flower like structure)	nanorods width	~ 60 nm (S5)
$Mn_xV_2O_5$/MWCNT	coating thickness	~ 2 to 10 μm (S6)
$Mn_xV_2O_5$ nanoflakes/platelets	thickness	~ 5 -15 nm (S6)
$Mn_xV_2O_5$ nanoflake/platelets	length	~ 150 nm (S6)

III. EDXS

The EDXS images (Fig.5) at high resolution of platelets like morphology in sample S6 ($Mn_xV_2O_5$/MWCNTs/felt). The chemical elemental distributions are shown in particular colours as shown in second raw. The platelets like morphology has higher amount of Mn atom % ($\sim$ 45%) on MWCNT's network.

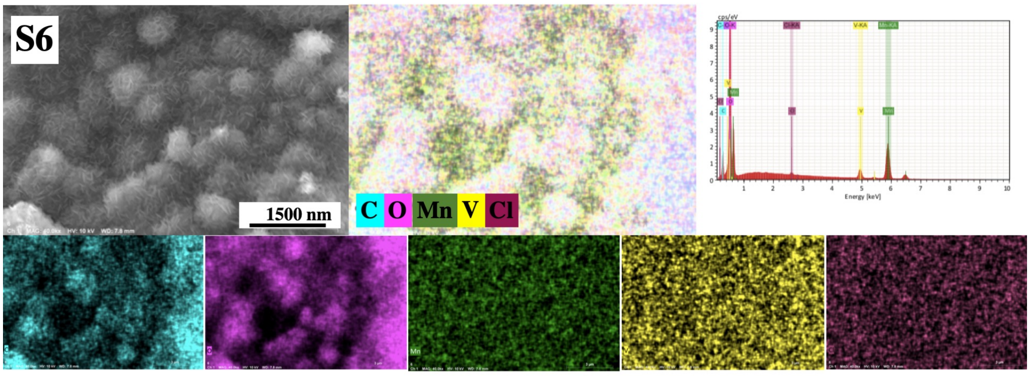

FIG. 5: The high resolution EDXS image of platelets like morphology of sample S6($Mn_xV_2O_5$/MWCNTs/felt) respectively.

In Tab.III the atomic (At%) of C, O, V and Mn elements present on sample surface area (6x4 mm size) (covering almost the whole sample surface carbon fibres) are shown. The chlorine and cobalt are found in very little amount, i.e., 0.3 to 2 at.%. The source of chlorine is the acid etching and cobalt came from the catalyst used during the MWCNT deposition.

TABLE III: Atomic % of C, O, V, Mn and Cl/Co ratio on 6×4 mm size surfaces.

Samples	**C%**	**O%**	**V%**	**Mn%**	**Cl/Co**
S1 (V_2O_5/felt)	83.0	10.0	7.0	-	-
S2 (V_2O_5/MWCNTs/felt)	87.0	9.0	2.0	-	2
S3 (MnO_2/felt)	17.0	44.0	-	37.0	2.0
S4 (MnO_2/MWCNT/felt)	44.0	35.0	-	20.0	1.0
S5 ($Mn_xV_2O_5$/felt)	82.0	13.0	1.0	4.0	0.3
S6 ($Mn_xV_2O_5$/MWCNT/felt)	63.0	21.0	1.0	15.0	0.5

IV. CARBON RAMAN SHIFT IN CM^{-1} VALUES

The carbon Raman bands of bare felt and MWCNTs/felt substrate samples are shown in Fig. 6. Where all the possible carbon bands positions are reported and their peak values in cm^{-1} are reported in Table IV.

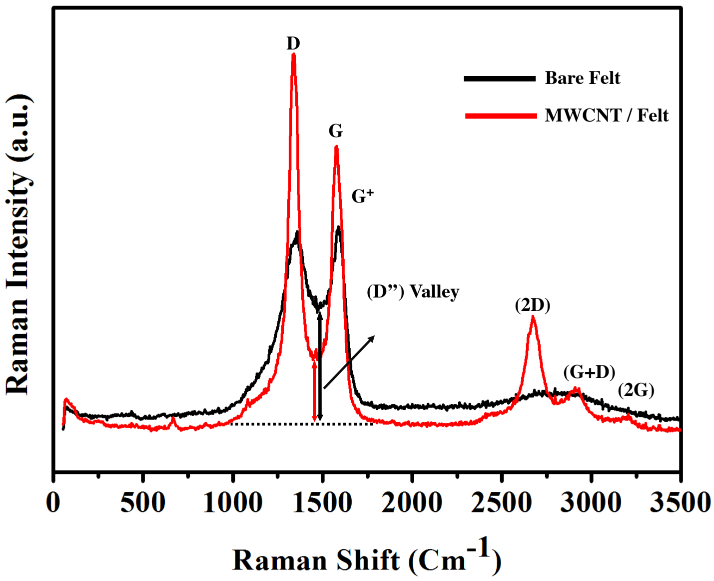

FIG. 6: The micro-Raman scattering bands of bare felt and MWCNTs/felt substrates respectively.

TABLE IV: Carbon Raman band shift (cm^{-1}) of felt substrate, MWCNTs/felt, S2 (V_2O_5/MWCNTs/felt), S4 (MnO_2/MWCNT/felt) and S6 ($Mn_xV_2O_5$/MWCNT/felt)

Samples	**D**	**D"**	**G**	**G+**	**2D/G'**	**G+D**	**2G,(G+D')**	$I_{D''}/I_G$	I_D/I_G	I_{2D}/I_G
felt	1357.53	1503.65	1589.16	-	-	-	-	0.50	0.97	0.10
MWCNTs/felt	1339.94	1513.05	1572.29	1604.29	2671.85	2926.28	3204.88	0.21	1.35	0.24
S2 (MnO_2/felt)	1344.98	1503.98	1586.60	1617.92	2689.99	2934.32	3215.49	0.21	1.07	0.42
S4 (MnO_2/MWCNT/felt)	1336.93	1477.90	1575.20	1603.15	2689.96	2906.17	3170.39	0.16	1.71	0.25
S6 ($Mn_xV_2O_5$/felt)	1334.19	1527.55	1569.36	1604.20	2664.09	2912.43	3197.47	0.12	1.25	0.34

Empirical formula for Crystallite size (L_a) calculation,

$$L_a = \frac{19.224}{\frac{I_D}{I_G}} \tag{1}$$

Where, L_a is the crystallite size in nm, λ is the wavelength of laser light source used in Raman scattering (λ 532 nm), I_D/I_G ratio is calculated from Raman scattering experiment

(From Table IV).

Empirical formula for bond length (R) in $\mathring{A}$ and bond order (S) by Raman frequencies [42]

$$R(\mathring{A}) = \frac{[-\ln \frac{\omega}{21349}]}{1.9176} \quad (2)$$

$$S = (0.2912 \ln \frac{21349}{\omega})^{-5.1} \quad (3)$$

Where, ω is Raman wavenumbers in cm^{-1}

V. XRD PATTERN

The XRD pattern was recorded for the bare felt, vanadium and manganese oxides with and without MWCNT. From the XRD results, the 2θ angles at 25.30, 42.36 and 52.78 are related to 002, 100 and 101 planes respectively that are assigned to only graphitic carbon felt properties from both felt and MWCNT/felt substrates. Thus, the XRD was not able to detect the material phases.

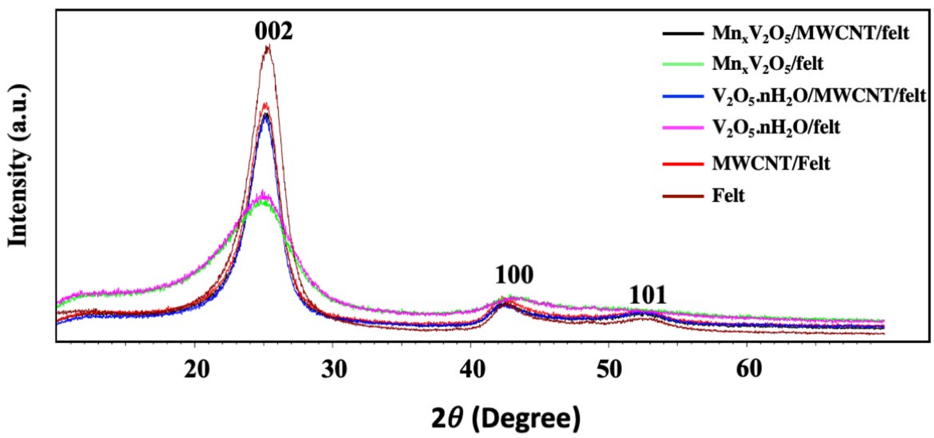

FIG. 7: The XRD pattern of bare felt and MWCNT/felt substrates, MnO_2/felt (S3), $V_2O_5.nH_2$/MWCNT/felt, $Mn_xV_2O_5$/felt and $Mn_xV_2O_5$/MWCNT/felt electrodes respectively.

VI. XPS ANALYSIS

The binding energy (B.E) of C1s, O1s, V2p and Mn2p core levels, calculated by fitting by Fityk software using Voigt function, are shown in Table V.

TABLE V: The binding energy (B.E.) values of C1s, O1s, V2p and Mn2p for respective samples

Samples	**C1s**	**O1s**	**V2p$_{3/2}$**	**Mn2p**
S1 (V_2O_5/felt)	284.6, 289.3	529.2, 530.8, 533.8	516.9	-
S2 (V_2O_5/MWCNTs/felt)	284.6, 286.4	529.4, 531.3, 533.3	517.0	-
S3 (MnO_2/felt)	284.6, 286.6	529.5, 531.9, 534.9	-	635.9, 641.0, 644.8
S4 (MnO_2/MWCNT/felt)	284.6, 286.5	529.2, 530.6, 532.9	-	641.1, 643.0, 645.3
S5 ($Mn_xV_2O_5$/felt)	284.5, 286.0	530.2, 532.2	517.1	635.7, 640.1, 645.1
S6 ($Mn_xV_2O_5$/MWCNT/felt)	284.5, 286.3	530.5, 532.8	517.31	636.2, 640.3, 646.0

VII. CHARGE DISCHARGE VS. TIME CURVES

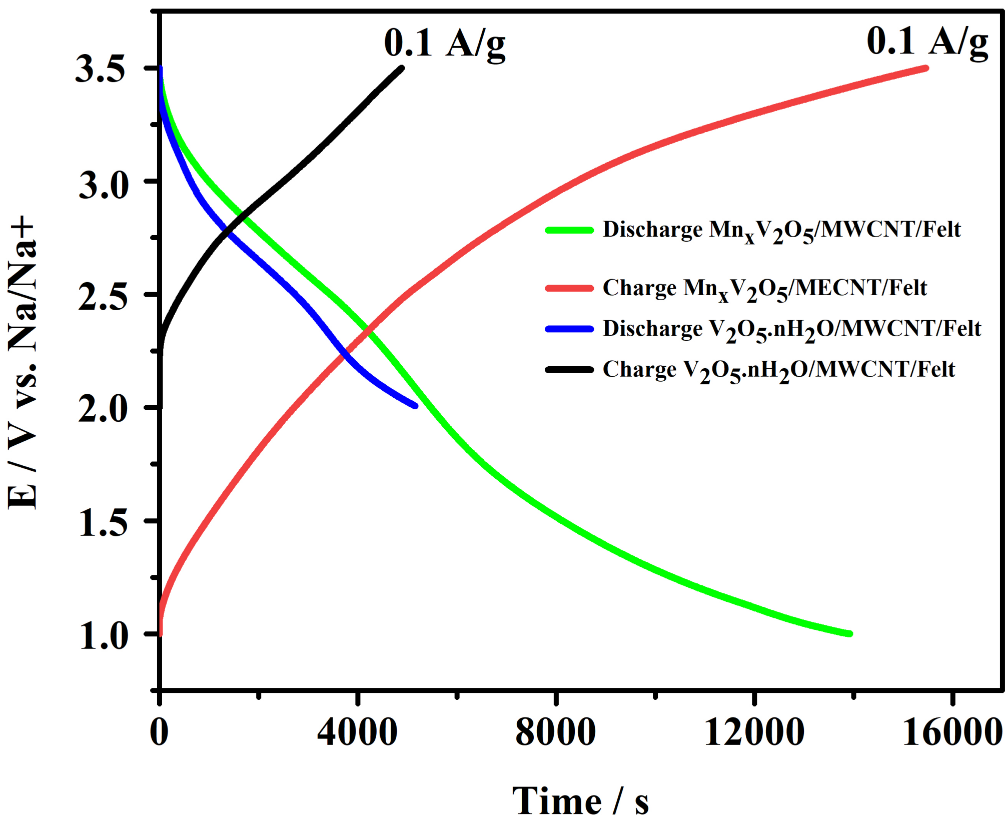

FIG. 8: The charge/discharge curve of $V_2O_5.nH_2O$/MWCNT/Felt and $Mn_xV_2O_5$ /MWCNT/Felt samples with respect to time (sec.).

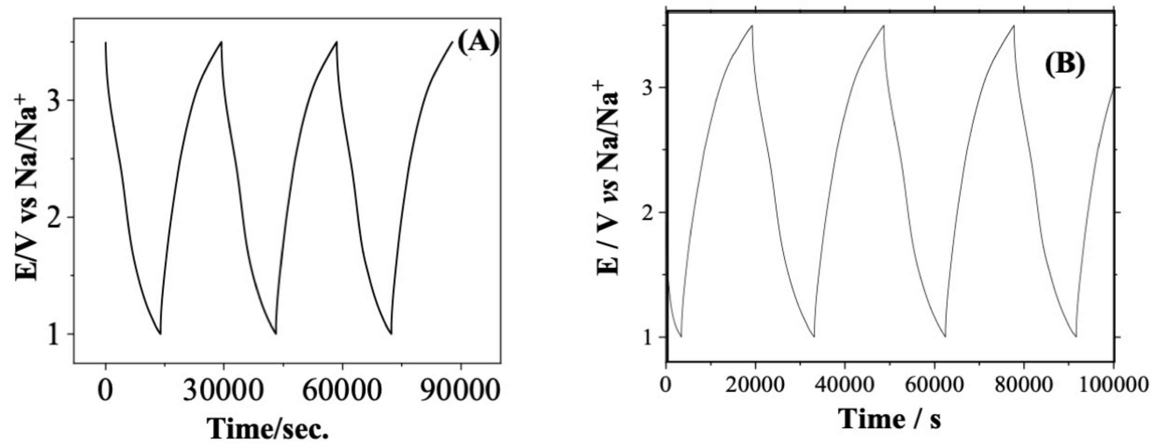

FIG. 9: Potential (E/Na/Na$^+$) versus Time (sec.) charge/discharge curves, $V_2O_5.nH_2O$/MWCNT/Felt (A) and $Mn_xV_2O_5$/MWCNT/Felt (B).

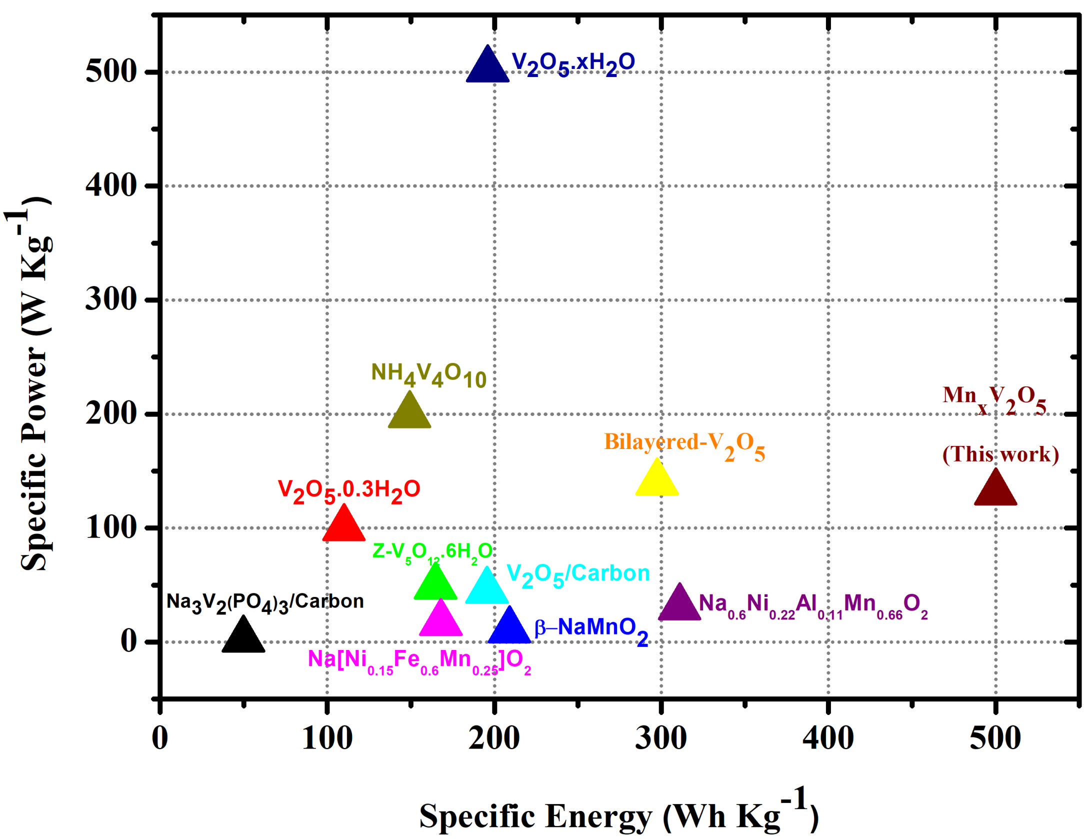

FIG. 10: The comparative Specific Energy density ($Wh.Kg^{-1}$) versus Specific Power density ($W.Kg^{-1}$) plot for Table 1, reported.