# High Power and Long Cycling Stability Supercapacitor Based on PANI/Mn<sub>2</sub>CoO<sub>4</sub> Nanohybrid

## M. Shanmugavadivel<sup>1</sup>, M. Subramanian<sup>1\*</sup> and V. Dhayabaran<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, H. H. Rajah's College, Pudukkottai, Tamil Nadu, India <sup>2</sup>Department of Chemistry, Bishop Heber College, Tiruchirapalli, Tamil Nadu, India \*Corresponding authors: msnhhrc@gmail.com; violetstaff@yahoo.co.in

> Received 16/10/2023; accepted 20/01/2024 https://doi.org/10.4152/pea.2025430403

#### Abstract

Nano-sized PANI/Mn<sub>2</sub>CoO<sub>4</sub> hybrid was successfully synthesized by diluted polymerization method, for high power SC. The metal oxide incorporation significantly increased the polymer's crystallinity and electrochemical efficiency. PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrochemical evaluation showed enhanced energy, power density (2.28 and 762.6 W/kg<sup>-1</sup>, respectively), specific capacitance (470 Fg<sup>-1</sup>) and columbic efficiency of 87.1%, with long cycling stability up to 1000 cycles. NHP improved capacitive nature and power characteristics were achieved by the synergistic effect between PANI and Mn<sub>2</sub>CoO<sub>4</sub>.

Keywords: charge-discharge; energy storage; PANI/Mn<sub>2</sub>CoO<sub>4</sub>; SC.



#### **Graphical abstract**

## Introduction•

Unifying organic and inorganic materials enhances their electrical and conducting properties, and facilitates their usage in energy storage devices. Electron transmission due to oxidation or reduction in PANI chain increases its affinity to many chemical molecules, thus limiting its electrochemical performance. Spontaneous charge transfers interactions occurring in the polymer backbone are complex and difficult to control [1, 2]. A potential way of increasing PANI's electrochemical properties is to incorporate an inorganic substance into its matrix [3-9].

The combination of metal oxide nanomaterials and PANI has proved to provide SC electrodes with very high energy and power density, which possess synergistic properties that are absent in each individual component. The synergistic effect facilitates a path for electron density transformation through distinct reaction sites on the electrode surface, by controllable interactions. The drastic enhancement of electrochemical properties and charge-discharge characteristics of the hybrid material depend not only on the synergistic effect of the constituents but also on their combined morphology and interfacial characteristics [10, 11].

MnCo<sub>2</sub>O<sub>4</sub> has been reported as a potential material for energy storage [12-15], although its electrochemical performance is reduced at higher j values. So, there is the need to combine metal oxides with other materials, to improve their capacity and stability. Herein, NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub> was synthesized by a simple chemical polymerization method. Its structural properties were studied by various physicochemical characterization methods, such as FT-IR, X-RD and SEM. Electrochemical and charge-discharge results revealed PANI/Mn<sub>2</sub>CoO<sub>4</sub> enhanced SC potential.

#### **Experimental method**

## Synthesis of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub>

NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub> was synthesized by surfactant-assisted dilute polymerization method. The dopant Mn<sub>2</sub>CoO<sub>4</sub> nanomaterial was prepared by a solution combustion method reported in literature [16]. The monomer solution was prepared by dissolving 0.2 M pure aniline in 100 mL/1 N HCl. DBSA and triton X-100 (2:1 mole ratio) surfactants were added to it, and mechanically stirred for 1 h. Mn<sub>2</sub>CoO<sub>4</sub> (5 wt%) was suspended in 100 mL/1 N HCl, and stirred for 30 min. Then, these two solutions were mixed together and continuously stirred for 1 h. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was dissolved in a 1 M (50 mL) HCl solution, and added dropwise to the monomer-surfactant solution, with continuous stirring. The whole polymerization process was carried out in ice cold conditions (0-5 °C), and the stirring proceeded for about 6 h. The product was filtered and washed several times with distilled water, until the filtrate became colorless. Then, the solid hybrid polymer was rinsed with HCl aqueous solution and methyl alcohol. Finally, the

<sup>•</sup> The abbreviations list is on page 245.

green colored PANI/Mn<sub>2</sub>CoO<sub>4</sub> NHP were filtered and dried under dynamic vacuum, at 80 °C, for 8 h.

#### Preparation of the modified electrode

The slurry was prepared by mixing 80 wt% PANI/Mn<sub>2</sub>CoO<sub>4</sub> with 10 wt% carbon black and 10 wt% PVdF in NMP, respectively. Then, the mixture was uniformly coated on a clean surface (1 × 1 cm) of the stainless-steel plate. Chemically modified PANI/Mn<sub>2</sub>CoO<sub>4</sub> was heated at 70 °C, to remove the organic solvent, and then used as working electrode. Pt foil and SCE were the counter and reference electrodes, respectively. CV scan (Versa STAT MC Electrochemical Workstation - Princeton Applied Research) was performed at different SR (10, 25, 50 and 75 mV/s<sup>-1</sup>), with a wide E window from -0.2 to 0.6 V, in a 1 M KOH electrolyte solution. GCD tests were carried out at different j values, to study the cyclic stability and power characteristics of PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode. Capacitive properties, such as specific capacitance, columbic efficiency, power and energy density were calculated by standard equations reported in literature [17-19].

#### **Results and discussion**

Fig. 1 shows FT-IR spectra of PANI/Mn<sub>2</sub>CoO<sub>4</sub>. It is clear that the spectrum contains a number of characteristic vibrations originating from both Mn<sub>2</sub>CoO<sub>4</sub> dopant and PANI host.



Figure 1: FT-IR spectrum of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub>

N=Q=N ring vibration mode appeared at 1119 cm<sup>-1</sup>. C=C for quinonoid and benzenoid rings occurred at 1588 and 1399 cm<sup>-1</sup>, respectively [20-22]. The sharp intense peak that came at 612 cm<sup>-1</sup> was assigned to Co-O bonding, and confirmed  $Mn_2CoO_4$  incorporation into PANI matrix. Wider and broader band centers at 3417 cm<sup>-1</sup> were attributed to N–H

and O-H vibration stretching modes. This broad vibration confirmed hydrogen bond formation between Mn<sub>2</sub>CoO<sub>4</sub> nanoparticles and N–H groups of PANI [23].

However, peaks obtained in NHP from PANI/ $Mn_2CoO_4$  slightly shifted and are different from those in pure  $Mn_2CoO_4$  and PANI. This significant change in stretching vibrations suggests that there was an interaction between PANI and  $Mn_2CoO_4$ .

X-RD pattern of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub> is shown in Fig. 2. The intense peaks that appear in X-RD indicate that PANI's increased crystallinity was due to Mn<sub>2</sub>CoO<sub>4</sub> addition.



Figure 2: X-RD pattern of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub>

Most of the intense peaks usually obtained in the case of pure Mn<sub>2</sub>CoO<sub>4</sub> nanoparticles  $(2\theta = 31.8340, 34.4853, 36.3303, 47.6017 and 56.6575)$  are present in the hybrid material, which is consistent with standard JCPDS values (No. 26-0168). The peaks at 19.7, 23.4, 29.0, 31.3, 32.9, 38.6, 47.1 and 57.8° are characteristic from PANI (JCPDS No.53-1717) [24]. PANI amorphous nature was improved by Mn<sub>2</sub>CoO<sub>4</sub> incorporation into its matrix. The sharp peaks that appear in X-RD depict the high degree of crystallinity due to extended  $\pi$  conjugation in the hybrid polymer [25, 26]. The average particle size (D) was calculated using Debye-Scherrer eq. (1):

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where k is 0.9 (constant),  $\lambda$  is Cu-ka radiation wave length (1.5418 Å),  $\beta$  is FWHM in radians, and  $\theta$  is Bragg's diffraction angle at maximum intensity. PANI/Mn<sub>2</sub>CoO<sub>4</sub> average particle size (60 nm) was calculated from the most intense XR-D maxima, by applying this equation. SEM images of PANI/Mn<sub>2</sub>CoO<sub>4</sub> are shown in Fig. 3 ((a) and (b), where the particles are clearly seen, highly aggregated, and have a porous nature. M. Shanmugavadivel et al. / Portugaliae Electrochimica Acta 43 (2025) 237-248



Figure 3: SEM images of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub>.

The average grain size was estimated to vary from 40 to 100 nm. The addition of nanosized  $Mn_2CoO_4$  to the PANI matrix reduced its crystalline size, and caused agglomeration. The uniformity of PANI/Mn\_2CoO\_4 individual particles was disturbed due to particle aggregation. The hybrid polymer core was made up of PANI, and its surface had encapsulated  $Mn_2CoO_4$ . The interaction between  $Mn_2CoO_4$  and PANI prevented the polymer over aggregation during the hybrid formation, and facilitated a synergistic effect, which is a key factor in enhancing its electrochemical performance.

PANI/Mn<sub>2</sub>CoO<sub>4</sub> formation was confirmed from TEM images (Fig. 4 - (a) and (b).



Figure 4: TEM images of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub>.

TEM images show that NHP particles do not have a uniform size and shape, due to  $Mn_2CoO_4$  nanoparticles incorporation into PANI matrix, which significantly changed the material morphology and size.  $Mn_2CoO_4$  appeared as dark black particles well embedded into PANI matrix whole surface.

PANI/ $Mn_2CoO_4$  electrode capacitive properties were qualitatively evaluated by CV scanning, at different SR, in a 1 M KOH electrolyte solution, within E window from 0.2 to 0.8 V (Fig. 5a).



**Figure 5: (a)** CV of PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode in a 1 M KOH aqueous solution; **(b)** Plot of SR *vs.* specific capacitance.

CV results at all SR (10, 25, 50 and 75 mVs<sup>-1</sup>) are similarly shaped, with good reversibility, and confirm the electrode pseudo capacitive nature. However, CV curves did not have a regular rectangular shape [27], due to the large number of redox reactions by the conjugated bonds present in PANI's chain [28]. The peak current increased significantly when SR changed from 10 to 75 mV/s<sup>1</sup>, due to the confinement of the active material on the electrode.

A wide rectangular area in the CV indicates the higher electro capacitive nature of the PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode and its very high specific capacitance value. The CV forward and reverse sweeps confirm the existence of all three different forms of PANI. Fully reduced leucomeraldine was observed at negative E of -0.2 V. During the sweep towards positive E, leucomeraldine was oxidized and converted into emeraldine form, at E from 0.2 to 0.35 V. Further oxidation occurred at more positive E (from 0.5 to 0.6 V), and yielded pernigraniline, PANI completely oxidized form [29-32].

The resulting current under CV curves was used to calculate the active material capacitance values at all four SR. PANI/Mn<sub>2</sub>CoO<sub>4</sub> specific capacitance values were 470, 234, 170.5 and 141.5 Fg<sup>-1</sup>, respectively, at the SR of 10, 25, 50 and 75 mV/s<sup>-1</sup>, respectively.

Fig. 5b depicts PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode variation in its specific capacitance, with respect to SR. It was seen that specific capacitance values steadily decreased with increasing SR from 10 to 75 mV/s<sup>-1</sup>. E sweep was slow at the lower SR. This facilitated the diffusion of a greater number of ions into the electrode, which increased the utility of the active material present on its surface. The specific capacitance values observed at higher SR (25, 50 and 75 mV/s<sup>-1</sup>) were relatively much lower, due to quick E sweep,

which reduced ionic diffusion rate. The synergistic effect between  $Mn_2CoO_4$  and PANI accelerated the reaction rate at the electrode-electrolyte interface, which facilitated the occurrence of redox reactions [33].

Stability is the key factor for any electrode material that can be used commercially in SC applications. PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode electrochemical stability was evaluated by continuous cycling up to 1000 cycles, at a SR of 50 mV/s<sup>-1</sup>.

Fig. 6a shows CV curves of  $1^{st}$  and  $1000^{th}$  cycles of PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode operated within E window from -0.2 to 0.6 V.

X-RD shape was not distorted even after 1000 continuous cycles. This indicates that the loss of active material was much lower during the cycling and was not affected by the reactions occurring at the electrode surface.



**Figure 6: (a)** 1<sup>st</sup> and 1000<sup>th</sup> cycle of PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode in a 1 M KOH aqueous solution; **(b)** Plot of cycle number *vs*. specific capacitance.

Fig. 6b shows specific capacitance of PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode as a function of cycle number. The specific capacitance gradually rose during the initial cycles, and showed a 5% increase after 100 cycles. The brisk ionic diffusion on PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode surface increased the porosity level and, thus, the specific capacitance value [34]. After reaching the maximum at the 100<sup>th</sup> cycle, the specific capacitance value steadily decreased during consecutive cycles. The capacitance fading was weaker after 650 cycles, and almost flattened at the 1000<sup>th</sup> cycle. The decrease in capacitance was expected even after 1000 cycles, but its fading may be insignificant. The capacitance retained by the active electrode material after 1000 successive cycles was 96%. The repeated redox reactions continuously occured during the long cyclic process, and generated the swelling effect which led to PANI backbone slight degradation, reducing specific capacitance value [35, 36]. PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode hybrid material withstood about 1000 cycles without any significant decrease in capacitance, indicating its superior stability in energy storage applications. Mn<sub>2</sub>CoO<sub>4</sub> incorporation into PANI effectively increased the polymer material stability and its capacitance retention ratio.

Fig. 7a shows GCD profile of PANI/Mn<sub>2</sub>CoO<sub>4</sub> hybrid electrode at an E window from -0.2 to 0.6 V, with different j values. The linear charge-discharge curves clearly indicate PANI/Mn<sub>2</sub>CoO<sub>4</sub> perfect reversibility and capacitive nature.



**Figure 7: (a)** GCD curves of PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode in a 1 M KOH aqueous solution at different j values; (b) plot of cycle number *vs.* columbic efficiency.

The amount of charge stored on the PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode was calculated by integrating the amount of current discharged during a complete charge-discharge cycle. The specific discharge capacitance calculated from the charge-discharge curve was 141.2 Fg<sup>-1</sup>, at the SR of 75 mV/s<sup>-1</sup>, which indicated the high capacitive nature of the hybrid electrode, even at higher SR cycling. The energy and power density measured at j of 2 mA/cm<sup>-2</sup> were 2.28 and 762.6 wk/g<sup>-1</sup>, respectively. PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode energy density was lower than that from the values of pure Mn<sub>2</sub>CoO<sub>4</sub> electrode reported in literature. The decrease in PANI/Mn<sub>2</sub>CoO<sub>4</sub> energy density was mainly due to the short discharging time during the cycling. However, its measured power density value was much higher than that from bare PANI [37, 38] and metal oxide doped PANI nanocomposites [39, 40].

The relation between the columbic efficiency and cycle number is shown in Fig. 6b. The columbic efficiency of the PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode after 1000 cycles was found to be 87.1%, which shows its high charge efficiency and superior electron transfer rate, even after 1000 cycles.

#### Conclusion

This work described the synthesis of NHP from PANI/Mn<sub>2</sub>CoO<sub>4</sub>, by a surfactant assisted chemical polymerization method. Physicochemical methods such as X-RD, FT-IR and SEM were employed to characterize PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode. Its highest capacitance value was 470 Fg<sup>-1</sup>, at a SR of 10 mV/s<sup>-1</sup>. The electrode also displayed a maximum energy density of 2.28 Wh/kg<sup>-1</sup> and a maximum power density of 762.6 W/kg<sup>-1</sup>, at j of 2 A/g<sup>-1</sup>. This power density value was higher than that of pure PANI or bare metaloxide-based SC. PANI/Mn<sub>2</sub>CoO<sub>4</sub> electrode superior

electrochemical performance was due to the surface activation induced by the synergistic contribution between them.

## Acknowledgements

The authors gratefully acknowledge the help of Prof. S. Navaneethan.

## **Conflict of interest**

The authors of this manuscript never received any funding, grants and support from the persons, agencies, industrial or commercial parties and declare no conflict of interest.

# Authors' contributions

**M. Shanmugavadivel**: sample preparation; carried out the experiment and performed calculations with results. **M. Subramanian**: designed and developed the research work; wrote the manuscript with support from authors. **V. Dhayabaran**: supervised and validated the research findings.

## Abbreviations

A/g: applied current (A)/amount of electrode material (g) **CV**: cyclic voltammetry DBSA: dodecyl benzene sulphonic acid E: potential **Fg**<sup>-1</sup>: specific capacitance FT-IR: Fourier transform infrared spectroscopy FWHM: full width of half-maximum **GCD**: galvanostatic charge discharge HCl: hydrochloric acid **j**: current density JCPDS: Joint Committee on Powder Diffraction Standards KOH: potassium hydroxide Mn<sub>2</sub>CoO<sub>4</sub>: manganese cobalt oxide (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>: ammonium persulphate **NHP**: nanohybrid particles NMP: N-methyl-2-pyrrolidine **PANI**: polyaniline **PVdF**: polyvinylidene difluoride redox: reduction-oxidation reaction SC: supercapacitor SCE: saturated calomel electrode **SEM**: scanning electron microscopy SR: scan rate **TEM**: transmission electron microscopy **XRD**: X-ray diffraction Wh/kg<sup>-1</sup>: gravimetric energy density

#### References

- 1. MacDiarmid AG, Epstein A. Polyanilines: a novel class of conducting polymers. J Faraday Discuss Chem Soc. 1989;88:317-332. https://doi.org/10.1039/DC9898800317
- 2. Shirota Y, Kageyama H. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. Chem Rev. 2007;107:953-1010. https://doi.org/10.1021/cr050143+
- 3. Ponzio EA, Benedetti TM, Torresi RM. Electrochemical and morphological stabilization of  $V_2O_5$  nanofibers by the addition of polyaniline. Electrochim Acta. 2007;52:4419-4427. https://doi.org/10.1016/j.electacta.2006.12.023
- 4. Malta M, Torresi RM. Electrochemical and kinetic studies of lithium intercalation in composite nanofibers of vanadium oxide/polyaniline. Electrochim Acta. 2005;50:5009-5014. https://doi.org/10.1016/j.electacta.2005.05.035
- Li G, Zhang C, Peng H et al. One-Dimensional V<sub>2</sub>O<sub>5</sub>@ Polyaniline Core/Shell Nanobelts Synthesized by an in situ Polymerization Method. Macromol Rapid Commun. 2009;30:1841-1845. https://doi.org/10.1002/marc.200900322
- Sui Y, Ma Y, Gao Y et al. PANI/MoO<sub>3</sub> xshell-core composites with enhanced rate and cycling performance for flexible solid-state supercapacitors and electrochromic applications. New J Chem. 2021;45:10654-10663. https://doi.org/10.1039/D1NJ01157J
- Ling X, Zhang G, Long Z et al. Core-shell structure g-MnO<sub>2</sub>-PANI carbon fiber paper-based flexible electrode material for high performance supercapacitors. J Ind Eng Chem. 2021;99:317-325. https://doi.org/10.1016/j.jiec.2021.04.044
- 8. Shao, Niu Y, Li B et al. Binary nanosheet frameworks of graphene/polyaniline composite for high-areal flexible supercapacitors. Mater Chem Phys. 2021;273:125128. https://doi.org/10.1016/j.matchemphys.2021.125128
- Gupta A, Sardana S, Dalal et al. Nanostructured Polyaniline/Graphene/Fe<sub>2</sub>O<sub>3</sub> Composites Hydrogel as a High-Performance Flexible Supercapacitor Electrode Material. ACS Appl Energy Mater. 2020;3:6434-6446. https://doi.org/10.1021/acsaem.0c00684
- Karim MR, Yeum JH, Lee MS et al. Preparation of conducting polyaniline/TiO<sub>2</sub> composite submicron-rods by the γ-radiolysis oxidative polymerization method. React Funct Polym 2008;68:1371-1376. https://doi.org/10.1016/j.reactfunctpolym.2008.06.016
- Conn C, Sestak S, Baker AT et al. A Polyaniline-Based Selective Hydrogen Sensor. Electro Analy. 1998;10:1137-1141. https://doi.org/10.1002/(SICI)1521-4109(199811)10:16%3C1137:AID-ELAN1137%3E3.0.CO;2-1
- 12. Liu Y, Yan C, Wang G et al. Achieving Ultrahigh Capacity with Self-Assembled Ni(OH)<sub>2</sub> Nanosheet-Decorated Hierarchical Flower-like MnCo<sub>2</sub>O<sub>4.5</sub>. ACS Appl Mat Interf. 2019;11:9984-9993. https://doi.org/10.1021/acsami.8b21803
- 13. Liu Z, Teng F, Yuan C et al. Highly Uniform MnCo<sub>2</sub>O<sub>4</sub> Hollow Spheres-Based All-Solid-State Asymmetric Micro-Supercapacitor via a Simple

Metal-Glycerate Precursor Approach. Ener Technol. 2019;7(9):1900314. http://dx.doi.org/10.1002/ente.201900314

- Boopathi RR, Parthibavarman M. Hetero-structure arrays of MnCo<sub>2</sub>O<sub>4</sub> nanoflakes@nanowires grown on Ni foam: Design, fabrication and applications in electrochemical energy storage. J Alloys Compd. 2019;811: 152084. https://doi.org/10.1016/j.jallcom.2019.152084
- 15. Gao Y, Xia Y, Wan H et al. Enhanced cycle performance of hierarchical porous sphere MnCo<sub>2</sub>O<sub>4</sub> for asymmetric supercapacitors. Electrochim Acta. 2019;301:294-303. https://doi.org/10.1016/j.electacta.2019.01.173
- 16. Shanmugavadivel M, Dhayabaran V, Subramanian M. Fabrication of high energy and high power density supercapacitor based on MnCo<sub>2</sub>O<sub>4</sub> nanomaterial. J Phys Chem Solids. 2019;133:15-20. https://doi.org/10.1016/j.jpcs.2019.04.029
- Hatchett DW, Josowicz M, Janata J. Acid Doping of Polyaniline: Spectroscopic and Electrochemical Studies. J Phys Chem B. 1999;103:10992-10998. https://doi.org/10.1021/JP991110Z
- Prasad KR, Munichandraiah N. Fabrication and evaluation of 450 F electrochemical redox supercapacitors using inexpensive and high-performance, polyaniline coated, stainless-steel electrodes. J Power Sour. 2002;112:443-451. https://doi.org/10.1016/S0378-7753(02)00419-6
- 19. Kim IJ, Yang S, Moon SI et al. Electrochemical characteristics of electric double layer capacitor with sheet type polarizable electrode. J Power Sour. 2007;164:964-967. https://doi.org/10.1016/j.jpowsour.2006.11.089
- 20. Wei Y, Hsueh KF, Jang G. A study of leucoemeraldine and effect of redox reactions on molecular weight of chemically prepared polyaniline. Macromolecules. 1994;27:518-525. https://doi.org/10.1021/ma00080a028
- Afzal AB, Javed AM, Nadeem M et al. Investigation of Structural and Electrical Properties of Polyaniline/Gold Nanocomposites. J Phys Chem C. 2009;113:17560-17565. https://doi.org/10.1021/jp902725d
- 22. Dong Y, Zhao Z, Wang Z et al. Dually Fixed SnO<sub>2</sub> Nanoparticles on Graphene Nanosheets by Polyaniline Coating for Superior Lithium Storage. ACS Appl Mater Interf. 2015;7:2444–2451. https://doi.org/10.1021/am506818h
- 23. Han MG, Cho SK, Oh SG et al. Preparation and characterization of polyaniline nanoparticles synthesized from DBSA micellar solution. Synth Met 2002;126:53-60. https://doi.org/10.1016/S0379-6779(01)00494-5
- 24. PCPDFWIN Version 2.4, JCPDS-ICDD 2003.
- 25. Bhaiswar JB, Salunkhe MY, Dongre S. Synthesis, Characterization, Thermal Stability and D.C. Electrical Conductivity of Pani/Pbs Nanocomposite. Int J Compos Mat. 2013;3:115-121. https://doi.org/10.5923/j.cmaterials.20130305.01
- 26. Subramanian E, Ramlakshmi RD, Vijayakumar N et al. Hybrid composite materials of *Anatase titania* and conducting polyaniline: properties and chemical sensor application. Ind J Eng Mat Sci. 2012;19:237-244. http://nopr.niscpr.res.in/handle/123456789/14651

- 27. Liu J, Zhou M, Fan LZ et al. Porous polyaniline exhibits highly enhanced electrochemical capacitance performance. Electrochim Acta. 2010;55:58195822. https://doi.org/10.1016/j.electacta.2010.05.030
- Xu JJ, Wang K, Zu SZ et al. Hierarchical Nanocomposites of Polyaniline Nanowire Arrays on Graphene Oxide Sheets with Synergistic Effect for Energy Storage. ACS Nano. 2010;4:5019-5026. https://doi.org/10.1021/nn1006539
- 29. Zhang X, Ji L, Zhang S et al. Synthesis of a novel polyaniline-intercalated layered manganese oxide nanocomposite as electrode material for electrochemical capacitor. J Power Sour. 2007;173(2):1017-1023. http://dx.doi.org/10.1016/j.jpowsour.2007.08.083
- Kaneko M, Kaneto K. Deformation of Poly(o-methoxyaniline) Film Induced by Polymer Conformation on Electrochemical Oxidation. Polymer. 2001;33:104-107. https://doi.org/10.1295/polymj.33.104
- 31. Pouget JP, Hsu CH, Mac Diarmid AG et al. Structural investigation of metallic PAN-CSA and some of its derivatives. Synth Metals. 1995;69:119-120. https://doi.org/10.1016/0379-6779(94)02382-9
- 32. Inamdar AI, Young SK, Jae SS et al. Supercapacitive Characteristics of Electrodeposited Polyaniline Thin Films Grown on Indium-doped Tin-oxide Substrates. J Korean Phys Soc. 2011;59(1):145-149. https://doi.org/10.3938/jkps.59.145
- 33. Wu CG, Yeh YR, Chen JY et al. Electroless surface polymerization of ordered conducting polyaniline films on aniline-primed substrates. Polymer. 2001;42:2877-2885. http://dx.doi.org/10.1016/S0032-3861(00)00582-6
- 34. Broughton JN, Brett MJ. Electrochemical Capacitance in Manganese Thin Films with Chevron Microstructure. Electrochem Solid State Lett. 2002;5:A279-A282. http://dx.doi.org/10.1149/1.1516412
- 35. Mitali S, Soma D, Monica D et al. A Study of Effect of Electrolytes on the Capacitive Properties of Mustard Soot Containing Multiwalled Carbon Nanotubes. Res J Chem Sci. 2011;1(3):109-113.
- Pico F, Ibanez J, Lillo-Rodenas MA et al. Understanding RuO<sub>2</sub>·xH<sub>2</sub>O/carbon nanofibre composites as supercapacitor electrodes. J Power Sour. 2008;176:417-425. https://doi.org/10.1016/j.jpowsour.2007.11.001
- 37. Guan H, Fan L, Zhang H et al. Polyaniline nanofibers obtained by interfacial polymerization for high-rate supercapacitors. Electrochim Acta. 2010;56:964968. http://dx.doi.org/10.1016%2Fj.electacta.2010.09.078
- Wang K, Huang J, Wei Z. Conducting Polyaniline Nanowire Arrays for High Performance Supercapacitors. J Phys Chem C. 2010;114:8062-8067. https://doi.org/10.1021/jp9113255
- 39. Bai M, Liu T, Luan F et al. Electrodeposition of vanadium oxide–polyaniline composite nanowire electrodes for high energy density supercapacitors. J Mater Chem A. 2014;2:10882-10888. https://doi.org/10.1039/C3TA15391F
- 40. Jaidev H, Jafri I, Mishra AK et al. Polyaniline–MnO<sub>2</sub> nanotube hybrid nanocomposite as supercapacitor electrode material in acidic electrolyte. J Mater Chem. 2011;21:17601-17605. https://doi.org/10.1039/C1JM13191E