Chromium Cobaltite Based Ternary Composite as Efficient Electrode Material for Hybrid Supercapacitors with Theoretical Investigation

Simran Kour, Pawanpreet Kour, A. L. Sharma*

Department of Physics, Central University of Punjab, Bathinda, Punjab, India-151401

*Corresponding author: alsharma@cup.edu.in

Supporting Information (SI)

1. Electrode preparation method

The electrodes were prepared by blending the synthesized active material, PVDF (binder), and carbon black (conductive element) in a ratio of 8:1:1 to get consistent slurry with the addition of N-Methyl-2-pyrrolidone (NMP). Nickel foam with area of 1 cm^2 was then coated with this slurry and dried at 60 ℃ overnight. The separator (Whatman paper) wetted by 6M KOH electrolyte was sandwiched between the two electrodes (cathode and anode) and pressed using a hydraulic press to get the desired cell configuration.

2. Electrochemical measurements

The capacitive response of the electrode material corresponding to a voltage window of -1 to +1V was evaluated from CV and GCD in 2-E configuration. The EIS analysis was carried out for 10^5-0.1 Hz of frequency at open-circuit potential. For asymmetric supercapacitor, the voltage range was 0-1.6 V. The Formulae used for determining various parameters such as specific capacitance, energy density, and power density has been provided in **Table S1**.

Table S1: Formulae used for finding various parameters.

Parameter	**Formula**	**Terms used**
Bragg's law	$2d\sin\theta = n\lambda$	'2θ' is bragg's diffraction angle, 'd' is inter-planar spacing, λ is the wavelength of X-ray, 'n' is an integer,.
Interplanar spacing	$d = \frac{1}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}}$	(a, b, c) are lattice parameters of the crystal, (hkl) are miller indices of lattice plane.
Crystallite size, D (Schherrer equation)	$D = \frac{K.\lambda}{\omega \times \cos\theta}$	'ω' is the FWHM, '2θ' is bragg's diffraction angle, K is a constant, λ is the wavelength of X-ray.
Specific capacitance, C_{sp} for single electrode (from CV)	$C_{sp} = \frac{\int I dV}{m \times \nu \times dV}$	'I' is the current, 'm' is the mass of active material, dV is the potential window, 'ν' is the scan rate.
Specific capacitance, C_{sp} for single electrode (from GCD)	$C_{sp} = \frac{2 \times I \times \Delta t}{m \times dV}$	'dt' is the discharging time, 'I' is the current, 'm' is the mass of active material.
Specific capacitance, C_{sp} for SSC/ASC (from GCD)	$C_{sp} = \frac{I \times \Delta t}{m \times dV}$	'dt' is the discharging time, 'I' is the current, 'm' is the mass of active material.
Energy density, E_d	$E_d = \frac{C_{sp} \times (dV)^2}{7.2}$	dV is the voltage window, 'C_{sp}' is the

(from GCD)		specific capacitance.
Power density, P_d (from GCD)	$P_d = \frac{E_d \times 3.6}{\Delta t}$	Δt is the discharging time, 'E_d' is the energy density.
Coulombic efficiency, η	$\eta = \frac{t_d \times 100}{t_c}$	't_c' is the charging time and 't_d' is the discharging time.
Response time, τ (from EIS)	$\tau = \frac{1}{\nu}$	'ν' is the frequency corresponding to phase angle $\theta = 45°$.

3. Results and Discussion

Table S2: Physico-chemical properties of activated carbon (AC).

Property	Value
Source	Coconut-shell
Appearance	Black powder
Molecular weight	12.01 g mol^{-1}
Median size	30-60 µm
Ignition temp.	842℉
Melting point	3550℃
Resistivity	1375 µΩ-cm

Table S3: XRD analysis for $CrCo_2O_4$ (CCO) microspheres.

Angle 2θ (degree)	Lattice plane (hkl)	Interplanar spacing, d (Å)	Crystallite size (nm)
18.86	(111)	4.69	8.71
31.01	(220)	2.88	15.06

36.42	(311)	2.46	10.49
44.37	(400)	2.03	11.57
54.88	(422)	1.67	8.71
58.61	(511)	1.57	9.66
64.46	(440)	1.44	10.44

Table S4: Identification of different functional groups from FTIR.

Wavenumber (cm^{-1})	Functional group	Reference
491.01	Cr-O	[1-3]
628.93	Co-O	[4]
745.44	C-H bending	[5]
1005.87	=C-N deformation (in-plane)	[6]
1143.70	C-N stretching	[6]
1156.65	C-O stretching	[6]
1273.92	C-H in-plane bending	[6, 7]
1424.69	C-H bending	[6]
1527.50	N-H bending	[6]
1575.47	C=C stretching	[8]
1624.21	C=C stretching	[7, 8]
2103.95	C ≡ C	[6]
2358.28	CO_2	[7]

3394.68	H-OH stretching	[7]

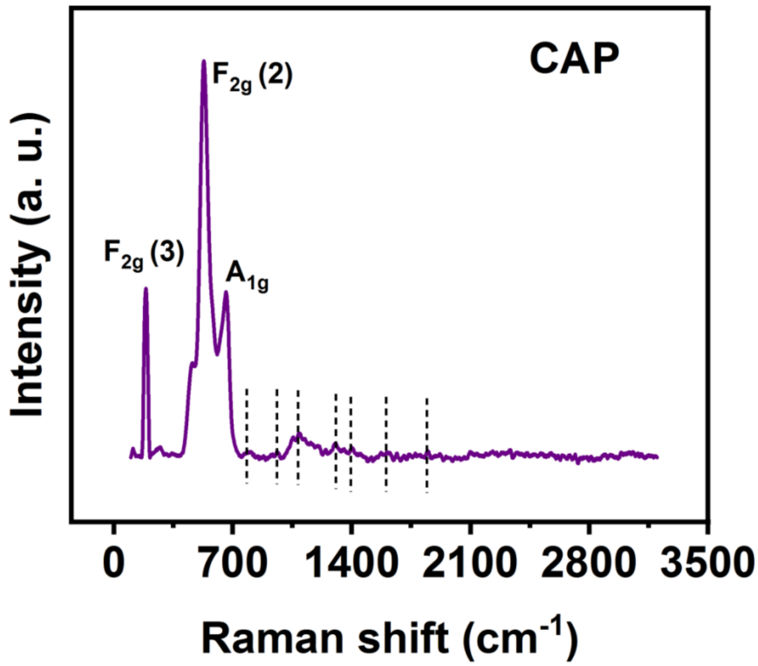

Fig. S1: Raman spectrum of CAP.

Table S5: Raman shift in CAP.

Symmetry	**Bond vibration**	**Raman shift (cm^{-1})**	**References**
δ(O-Co-O)	F_{2g}(3)	192.88	[9]
v (Cr-O)	F_{2g}(2)	527.18	[10]
v_s (Cr-O)	A_{1g}	663.13	[9, 10]
PPY ring	Polaron distortion	965.80	[11]
C-H	In plane bending	1053	[12, 13]
C-H	In plane bending	1093	[4]

C-N	Stretching	1220	14
PPY Ring	Stretching	1347	5
C=C	Asymmetric stretching	1418	14
C=C	Asymmetric stretching	1580	15

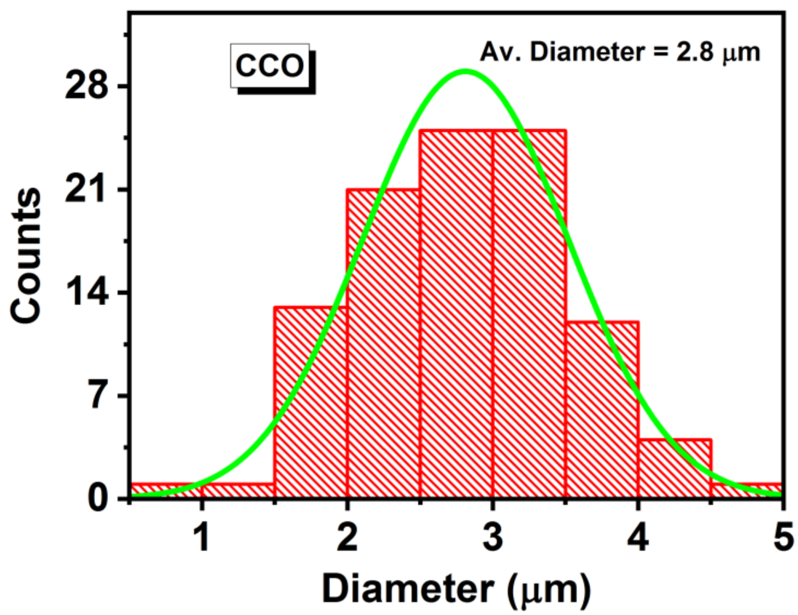

Fig. S2: Size distribution of CCO.

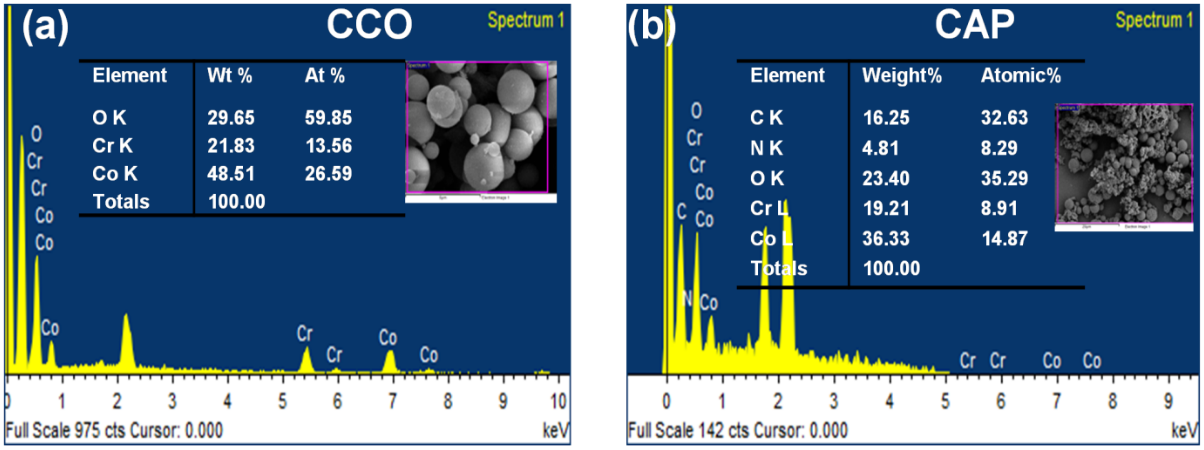

Fig. S3: EDS of **(a)** CCO and **(b)** CAP.

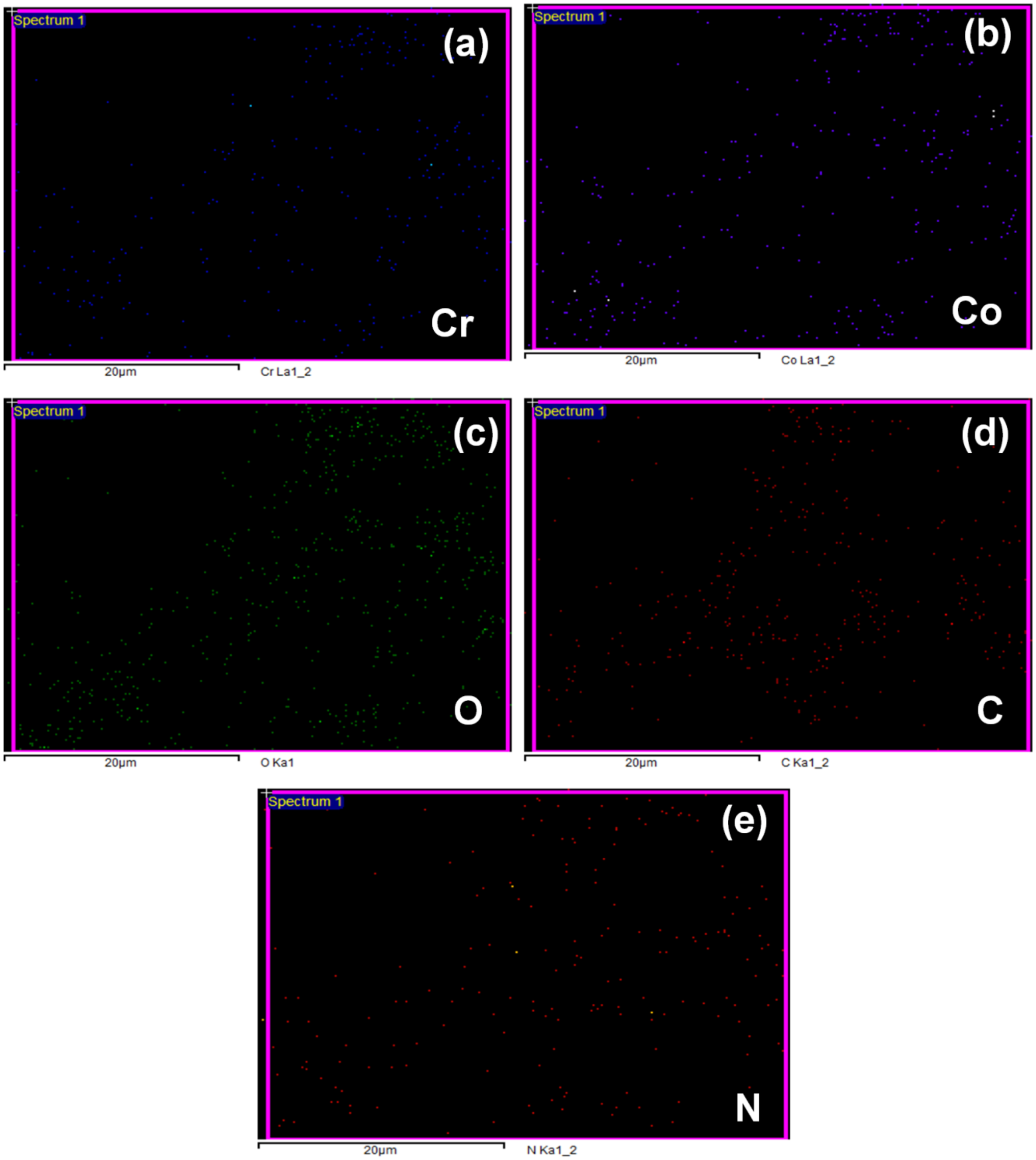

Fig. S4: Elemental mapping of CAP.

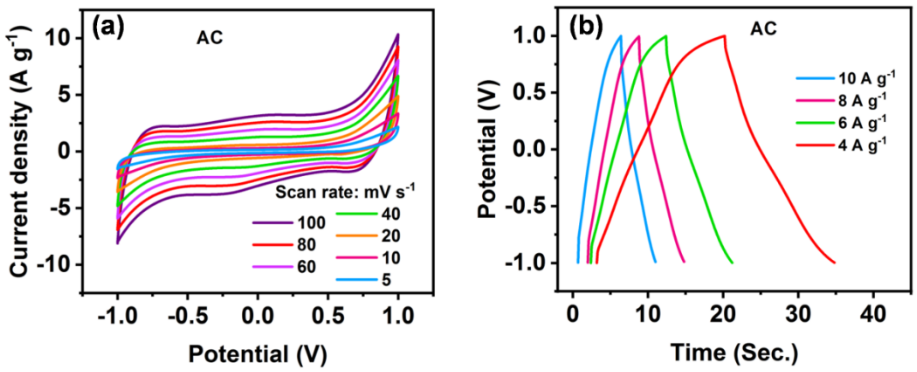

Fig. S5: (a) CV and **(b)** GCD curves of AC.

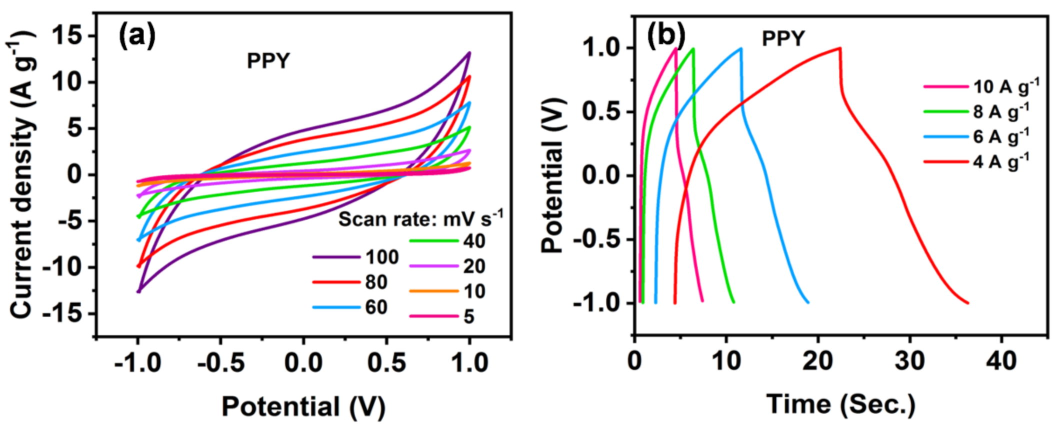

Fig. S6: (a) CV and **(b)** GCD curves of PPY.

Table S6: R_s and R_{ct} of CCO, CAC, and CAP.

Sample	CCO	CAC	CAP
R_s (Ω)	3.69	2.67	2.14
R_{ct} (Ω)	0.37	0.34	0.36

Table S7: Supercapacitive performance comparison of the prepared samples with literature.

Material	C_{sp}	**Voltage**	**ASC/SSC**	**E_d**	**Pd**	**Stability,**	**Reference**

	(Fg^{-1})	window (V)		(Wh kg^{-1})	(kW kg^{-1})	% (cycles)	
$MnCo_2O_4$-graphite@PPY	2364	0-1.6	ASC	25.7	16.1	85.5 (10,000)	[16]
$NiCo_2O_4$/NF@PPY	1717 C g^{-1}	0-1.6	ASC	68.9	1.77	89.2 (10,000)	[17]
$MgCo_2O_4$/PPY	988 (1 A g^{-1})	0-1.6	ASC	40.0	1.54	84.0 (10,000)	[18]
$NiCo_2O_4$/CNF@PPY	910 (1 A g^{-1})	0-1.5	ASC	40.8	0.73	88.0 (10,000)	[19]
$NiCo_2O_4$/Co_3S_4/MnS @PPY	2557 (1 A g^{-1})	0-1.6	ASC	81.1	0.80	83.6 (20,000)	[20]
$MnNi_2O_4$/PPY	304 (1 A g^{-1})	0-1.6	ASC	35.9	0.80	--	[21]
CC@$NiCo_2O_4$@PPY	1687 (1 A g^{-1})	0-1.5	ASC	46.5	0.72	80.0 (10,000)	[22]
$NiCo_2O_4$@PANI	561 (10 mV s^{-1})	0-1.2	ASC	6.4	0.28	86.2 (3,000)	[23]
$CoFe_2O_4$/PANI/GO	346.9 (1 A g^{-1})	0-1.2	SSC	69.3	5.98	79.0 (5,000)	[24]

$NiMoO_4$/rGO/PANI	1150 C g^{-1} (1 A g^{-1})	0-1.7	ASC	82.43	0.85	94.5 (10,000)	[25]
$CuCo_2O_4$/GO@PANI	312.7 (1 A g^{-1})	0-1.2	SSC	62.5	5.99	84.2 (5,000)	[26]
Fe-$MnCo_2O_4$@PPY	422.4 (2 mA cm^{-2})	0-1	SSC	519.9 mWh cm^{-2}	--	94.7 (7,000)	[27]
$CoCr_2O_4$/Ti_3C_2	417	-0.2-0.5	3-E	20.89	0.60	--	[28]
$NiCo_2O_4$/CF@PANI	369 mAh g^{-1}	0-1.5	ASC	60.60	2.32	--	[29]
$CoCr_2O_4$/Co-MOF	596.8 C g^{-1} (1 A g^{-1})	0-1.6	ASC	34.36	0.20	96.2 (5,000)	[30]
$CrCo_2O_4$/AC/PPY	991.25 (5 mV s^{-1}), 879.37 (4 A g^{-1})	0-1.6	HSC	97.77	1.6	76.75 (10,000)	This work

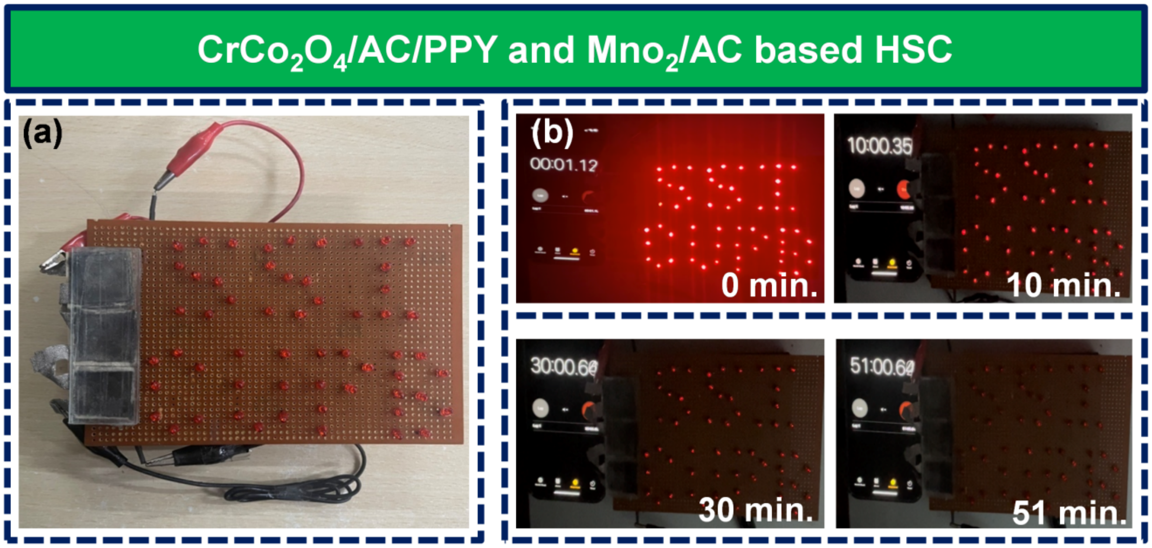

Fig. S7: (a) LED-setup for device testing; and **(b)** Digital images of glowing LED-panel at different times.

References

1. E. Berei, O. Ştefănescu, C. Muntean, B. Ţăranu and M. Ştefănescu, *Journal of Thermal Analysis and Calorimetry*, 2019, **138**, 1863-1870.
2. P. Choudhary, P. Saxena, A. Yadav, A. Sinha, V. Rai, M. Varshney and A. Mishra, *Journal of Superconductivity and Novel Magnetism*, 2019, **32**, 2639-2645.
3. A. Borhade, V. Bobade, D. Tope, J. Agashe and S. Kushare, *Journal of Inorganic and Organometallic Polymers and Materials*, 2021, **31**, 4670-4683.
4. P. Zhang, J. Liu, J. Wu, W. Wang, C. Zhou, S. Guo, S. Li, Y. Yang and L. Chen, *Materials Today Energy*, 2020, **17**, 100451.
5. R. A. Sutar, L. Kumari and M. MV, *Journal of Applied Physics*, 2021, **130**.
6. A. B. D. Nandiyanto, R. Oktiani and R. Ragadhita, *Indonesian Journal of Science and Technology*, 2019, **4**, 97-118.
7. R. Jin, Y. Meng, Y. Ma, H. Li, Y. Sun and G. Chen, *Electrochimica Acta*, 2016, **209**, 163-170.
8. J. Hu, M. Li, F. Lv, M. Yang, P. Tao, Y. Tang, H. Liu and Z. Lu, *Journal of Power Sources*, 2015, **294**, 120-127.
9. Z. Tian, C. Zhu, J. Wang, Z. Xia, Y. Liu and S. Yuan, *Journal of Magnetism and Magnetic Materials*, 2015, **377**, 176-182.
10. M. Kamran, K. Nadeem and M. Mumtaz, *Solid State Sciences*, 2017, **72**, 21-27.
11. H. S. Abdullah, *Int. J. Phys. Sci*, 2012, **7**, 5468-5476.
12. M. Gniadek, S. Malinowska, T. Rapecki, Z. Stojek and M. Donten, *Synthetic metals*, 2014, **187**, 193-200.
13. M. A. Farea, H. Y. Mohammed, P. W. Sayyad, N. N. Ingle, T. Al‐Gahouari, M. M. Mahadik, G. A. Bodkhe, S. M. Shirsat and M. D. Shirsat, *Applied Physics A*, 2021, **127**, 681.

14. G. Arteaga, M. Del Valle, M. Antilén, M. Romero, A. Ramos, L. Hernández, M. Arévalo, E. Pastor and G. Louarn, *International Journal of Electrochemical Science*, 2013, **8**, 4120-4130.
15. F. Wu, M. Sun, W. Jiang, K. Zhang, A. Xie, Y. Wang and M. Wang, *Journal of Materials Chemistry C*, 2016, **4**, 82-88.
16. F. Wang, X. Lv, L. Zhang, H. Zhang, Y. Zhu, Z. Hu, Y. Zhang, J. Ji and W. Jiang, *Journal of Power Sources*, 2018, **393**, 169-176.
17. R. BoopathiRaja and M. Parthibavarman, *Electrochimica Acta*, 2020, **346**, 136270.
18. S. Sathishkumar, M. Karthik, R. Boopathiraja, M. Parthibavarman, S. Nirmaladevi and S. Sathishkumar, *J Mater Sci.: Mater Electron* 2022, **33**, 21600-21614.
19. T. H. Ko, D. Lei, S. Balasubramaniam, M.-K. Seo, Y.-S. Chung, H.-Y. Kim and B.-S. Kim, *Electrochimica Acta*, 2017, **247**, 524-534.
20. L. He, Z. Guo, G. Wang and M. Li, *Journal of Energy Storage*, 2024, **79**, 110130.
21. A. Sathiyan, E. Elaiyappillai, S.-F. Wang, S. Dhineshkumar and P. M. Johnson, *New Journal of Chemistry*, 2024, **48**, 3080-3088.
22. J. Yu, D. Yao, Z. Wu, G. Li, J. Song, H. Shen, X. Yang, W. Lei, F. Wu and Q. Hao, *ACS Applied Energy Materials*, 2021, **4**, 3093-3100.
23. X. Li, H. Xie, Y. Feng, Y. Qu, L. Zhai, H. Sun, X. Liu and C. Hou, *Journal of Applied Polymer Science*, 2023, **140**, e54580.
24. S. Verma, T. Das, V. K. Pandey and B. Verma, *Journal of Molecular Structure*, 2022, **1266**, 133515.
25. H. M. Fahad, R. Ahmad, F. Shaheen, A. A. Ifseisi, M. H. Aziz and Q. Huang, *Electrochimica Acta*, 2024, 143756.
26. S. Verma, V. K. Pandey and B. Verma, *Synthetic Metals*, 2022, **286**, 117036.
27. Z. Chen, X. Zu, L. Chen, Y. Qi, W. Jian, Y. Wu, W. Zhang, X. Lin, G. Yi and Q. Liu, *ACS Applied Energy Materials*, 2022, **5**, 5937-5946.
28. R. Shafique, M. Rani, A. Mahmood, R. A. Alshgari, K. Batool, T. Yaqoob, N. K. Janjua, S. Khan, S. Khan and G. Murtaza, *International Journal of Energy Research*, 2022, **46**, 6689-6701.
29. S. K. Shinde, S. S. Karade, N. T. N. Truong, S. S. Veer, S. F. Shaikh, A. M. Al-Enizi, A. D. Jagadale, H. M. Yadav, M. S. Tamboli and C. Park, *Journal of Energy Storage*, 2024, **78**, 109960.
30. Q. Li, J. Zhou, S. Zhao, Y. Li, C. Chen, K. Tao, R. Liu and L. Han, *ChemElectroChem*, 2020, **7**, 437-444.