

Mn₃O₄ nanospheres@rGO architecture with Capacitive Effects on the High Potassium Storage Capability

Chandrasekaran Nithya^a, Palanivelu Vishnuprakash^a, Sukumaran Gopukumar^c*

^aDepartment of Chemistry, PSGR Krishnammal College for Women, Coimbatore – 641 004.

^bDepartment of Energy and Environment, National Institute of Technology, Tiruchirappalli – 620 015, India

^cCSIR-Network Institute of Solar Energy, CSIR-Central Electrochemical Research Institute, Karaikudi, India 630 006

Supporting Information

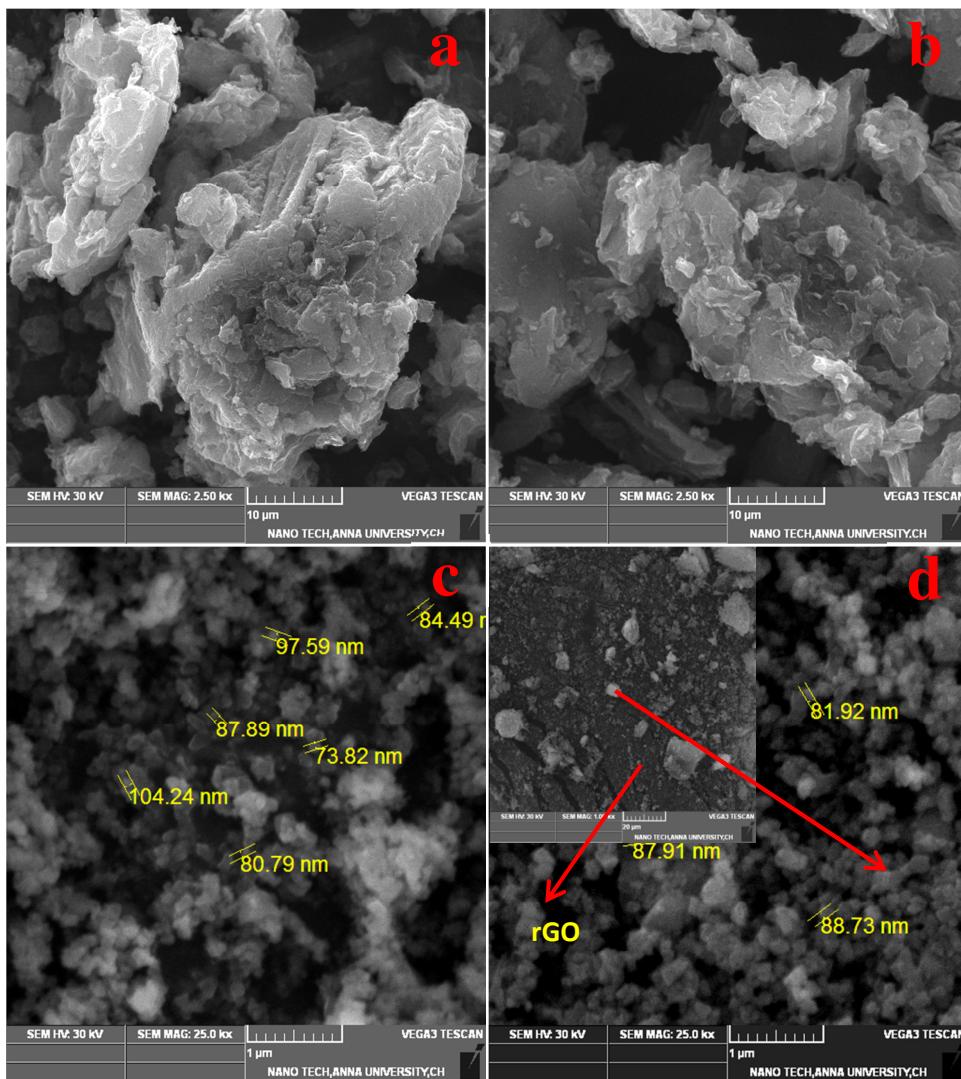


Fig. S1 SEM images of (a) GO (b) rGO (c) Mn_3O_4 (d) Mn_3O_4 @rGO (Inset in Fig. d – SEM image of Mn_3O_4 @rGO at low magnification).

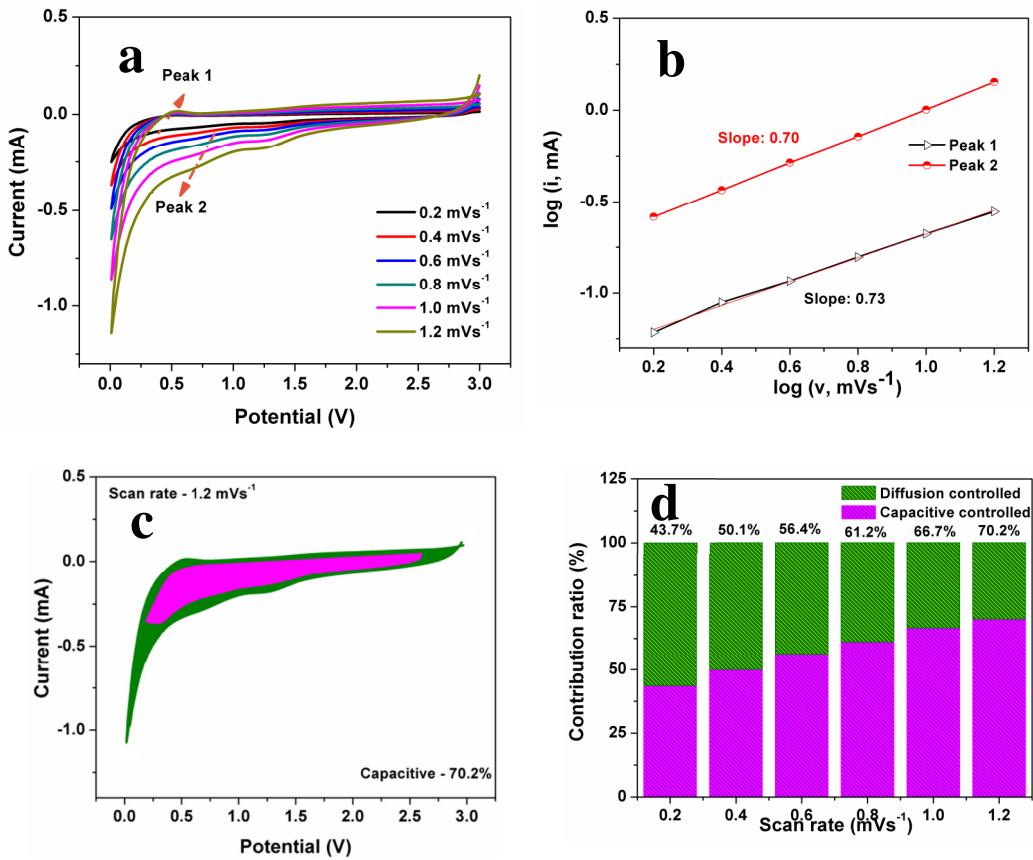


Fig. S2 (a) CV curves of Mn_3O_4 at various scan rates (b) $\log i$ vs. $\log v$ plots at oxidation and reduction state (c) Capacitive contribution Mn_3O_4 at 1.2 mVs^{-1} (d) Normalized contribution ratio of capacitive and diffusion controlled capacities of Mn_3O_4 at various scan rates.

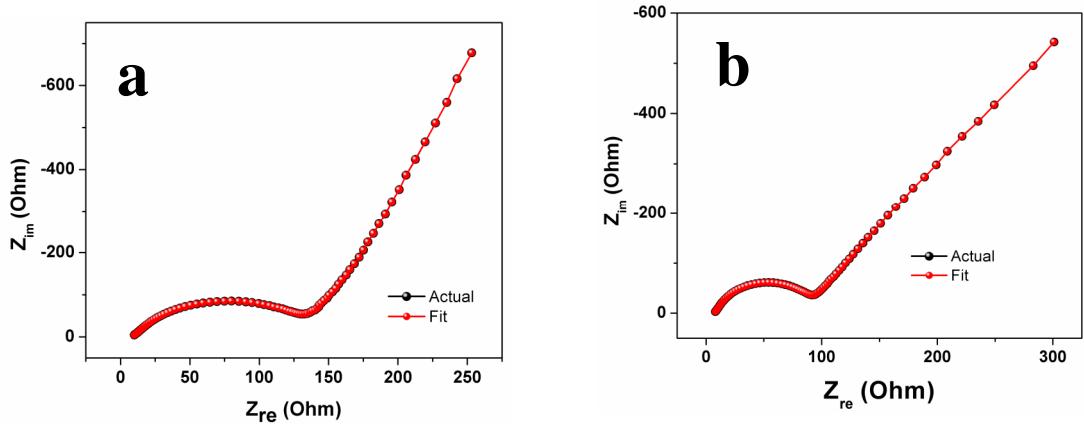


Fig. S3 Actual and fitted Nyquist plots of (a) Mn_3O_4 (b) $\text{Mn}_3\text{O}_4@\text{rGO}$

Table S1. Comparison of Mn_3O_4 as anode material for LIBs, NIBs and KIBs by various synthesis techniques.

S.No.	Electrode material	Current density (mA/g)	Specific capacity (mAh/g)	Number of cycles	Capacity retention after n^{th} cycle	Reference
1.	Mn_3O_4 microsphere composed of ultrathin nanosheets (Ethanol Thermal reduction Method) for LIBs	100	640	100	95.81	[1]
		2000	324	1000	85.27	
2.	Mn_3O_4 nanoparticles with P_{123} as surfactant (Solvothermal method) for LIBs	100	625.9	75	44.14	[2]
	Mn_3O_4 nanoparticles with HMTA as surfactant (Solvothermal method) for LIBs	100	234.7	75	15.57	
3.	$\text{Mn}_3\text{O}_4/\text{rGO}$ (Two step solution phase reaction) for LIBs	400	780	10	97.50	[3]
		1600	390	10	81.25	
	Pristine Mn_3O_4	40	115	10	41.08	

4.	Sponge like Nanosized Mn ₃ O ₄ (Precipitation method) for LIBs	234	780	40	86.66	[4]
5.	HCF/Mn ₃ O ₄ (HCF was prepared by acid treatment method and HCF/Mn ₃ O ₄ was prepared by insitu synthesis) for LIBs	200	835	100	89.8	[5]
		1000	652	240	66.52	
6.	Mn ₃ O ₄ /C microspheres (Solvothermal method) for LIBs	200	1032	500	80	[6]
		1000	848	500	78.16	
		1500	778	500	71.71	
7.	Graphene/Mn ₃ O ₄ (Graphene by Modified Hummer's method and Mn ₃ O ₄ by precipitation method) for LIBs	100	702	100	87.5	[7]
	Mn ₃ O ₄ for LIBs	100	171	100	37.4	
8.	Mn ₃ O ₄ vs LIBs (Selective dissolution method)	50	400	500	41.67	[8]
	Mn ₃ O ₄ vs NIBs	200	167	200	49.86	
	Mn ₃ O ₄ vs KIBs	100	156	100	41.66	
9.	Mn ₃ O ₄ @C (Hydrothermal reaction) for LIBs	40	473	50	38	[9]
	Mn ₃ O ₄ for LIBs	40	155	50	15.9	
10.	Mn ₃ O ₄ /rGO (6.9wt% of rGO) (Two step chemical reaction) for LIBs	1000	540	100	73.1	[10]
11	Mn₃O₄@rGO for KIBs (precipitation followed by ultrasonication)	500	704	500	90	Present work

References

1. L. Xu, X. Chen, L. Zeng, R. Liu, C. Zheng, Q. Qian, Q. Chen “Synthesis of hierarchical Mn₃O₄ microsphere composed of ultrathin nanosheets and its excellent long-term cycling performance for lithium-ion batteries” *J. Mater. Sci. Mater. Electron.* 2019, **30**, 3055-3060
2. Y. Yang, S. Yang, C. Feng, H. Zheng, Q. Xia “Solvothermal synthesis of Mn₃O₄ as an anode material for lithium ion batteries” *J. Electroceram.* **2018** <https://doi.org/10.1007/s10832-018-0171-9>
3. H. Wang, L. Cui, Y. Yang, H. S. Casolongue, J. T. Robinson, Y. Liang, Y. Cui, H. Dai “Mn₃O₄ -Graphene Hybrid as a High-Capacity Anode Material for Lithium Ion Batteries” *J. Am. Chem. Soc.* 2010, **132**, 13978-13980.
4. J. Gao, M. A. Lowe, H. D. Abruna “Sponge like nanosized Mn₃O₄ as a high-capacity anode material for rechargeable lithium batteries” *Chem. Mater.* 2011, **23**, 3223-3227.
5. D. Zhang, G. Li, J. Fan, B. Li, L. Li “In situ synthesis of Mn₃O₄ nanoparticles on hollow carbon nanofiber as high-performance lithium-ion battery anode” *Chem. Eur. J.* 2018, **24**, 9632-9638.
6. H. J. Peng, G. X. Hao, Z. H. Chu, J. Lin, X. M. Lin, Y. P. Cai “Mesoporous Mn₃O₄/C Microspheres fabricated from MOF template as advanced Lithium-Ion battery anode” *Cryst. growth and des.* 2017, **17**, 5881-5886.
7. J. G. Wang, D. Jin, R. Zhou, X. Li, X. R. Liu, C. Shen, K. Xie, B. Li, F. Kang, B. Wei “Highly flexible Graphene/Mn₃O₄ Nanocomposite membrane as advanced anodes for Li-Ion Batteries” *ACS Nano* 2016, **10**, 6227-6234.
8. C. Tang, F. Xiong, X. Yao, S. Tan, B. Lan, Q. An, P. Luo, L. Mai “Hierarchical Mn₃O₄/Graphene Microflowers Fabricated via a selective dissolution strategy for Alkali-Metal-Ion Storage” *ACS Appl. Mater. Interfaces* 2019, **11**, 14120-14125.

9. C. Wang, L. Yin, D. Xiang, Y. Qi “Uniform carbon layer coated Mn₃O₄ Nanorod anodes with improved reversible capacity and cyclic stability for Lithium Ion Batteries” *ACS Appl. Mater. Interfaces* 2012, **4**, 1636-1642.
10. S. Li, L. L. Yu, Y. T. Shi, J Fan, R. B. Li, G. D. Fan, W. L. Xu, J. T. Zhao “Greatly enhanced faradic capacities of 3D porous Mn₃O₄/G composites as Lithium-Ion Anodes and supercapacitors by C-O-Mn bonding” *ACS Appl. Mater. Interfaces* 2019, **11**, 10178-10188.

Table S2. The fitting results of electrochemical impedance spectroscopy of the rGO, pristine Mn₃O₄ and Mn₃O₄@rGO composite

Material	R _s (Ω)	R _{sf} (Ω)	R _{CT} (Ω)	C _{dl} (mF)
rGO	1.10	7.2	133.1	36.7
Mn ₃ O ₄	9.95	20.2	155.3	18.2
Mn ₃ O ₄ @rGO	8.04	9.8	92.7	55.2