Pristine and Doped Transition Metal oxides for Lithium Ion Batteries

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Abstract

Mixed transition metal oxides with adjustable composition and structures are widely used in electro chemical cell applications such as lithium-ion batteries and supercapacitors their high theoretical capacity, high energy density, high cyclic durability, and environment friendliness compared to mono metal oxides. Different routes like sol gel, combustion, solvothermal, sonication, hydrothermal are used for their synthesis. This chapter gives an overview of some of the key MTMOs in different structural and forms like layer, core-shall, nanorods, nanosheets etc and in the forms of composites with materials like PANI, rGO, CNT, CNF etc

Keywords: Mixed Transition Metal oxides, Energy storage, Li ion batteries

1. Introduction

Mixed transition metal oxides (MTMOs, also known as $A_xB_{3x}O_4$)-based electrode materials have been the subject of extensive research in recent years for electrochemical storage technology **[1-6]**. Lithium-ion batteries (LiB), and supercapacitors (SC) are used in portable electronics to EV's and HEV's. **[7-9].** Their structure and composition can be tuned, making them demand in electrochemical energy-storage devices. LiBs have high energy density, high power density, long cycle life, minimal self-discharge, and low temperature performance **[10]**. The selectivity of anode and cathode materials has a significant impact on how Lithium-ion battery function. Graphite and silicon graphite-based electrodes materials are used in commercial Lithium-ion battery cell pack (for anode side) and Lithium-iron phosphate, lithium manganese oxide, Lithium Cobalt oxide are used as a cathode. However, Graphite electrodes exhibit minimal theoretical capacity and generally subpar rate performance. Instead of using traditional graphite, transition metal oxides are used **[11].** The combination of oxides of the transition metals (**Fig 1**) is used in energy storage devices. The different Transition Metal oxides, Mixed Metal Oxides and Nanocomposite materials along with their synthesis procedures and application or performance discussed are listed in **Table 1**

2. Electrode materials for Li ion batteries

For lithium-ion batteries, transition metal oxides are seen as potential negative electrode materials. TMOs for anode materials including SnO_2, Mn_3O_4, Fe_2O_3, Co_3O_4 and ZnO have been the subject of substantial research by numerous groups up to this point **[12-16]**. The next generation of MTMO's, such as $ZnCo_2O_4$ **[17]**, $NiCo_2O_4$ **[18]** and $ZnMn_2O_4$ **[19]**, are becoming more and more important because to their high theoretical capacity, high energy density, high cyclic durability, environmental compatibility, and comparably low cost to Ni and Co species. These materials contain a lot of manganese species. The low oxidation potentials of Zn and Mn, provide another advantage. Lithium-ion battery can be substituted with potassium and sodium ions. The difficulties however they face is the insufficient anodic materials and therefore rely on biomass and waste materials **[20]**. Transition metal molybdates and phosphates like Cu-nickel molybdate (CuNiMo) showed high capacity. The high surface area and porous nature in $NiCo_2O_4$/rGO on Ni foam gives more active sites with high energy density. The porous carbon network acts as nucleation sites for Nanorod network of $NiCo_2O_4$/Au which are used as flexible/transparent supercapacitors with good energy density along with power density **[21-24].**

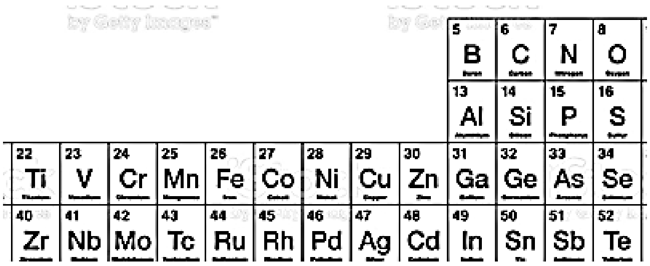


Fig 1. Transition metals in the Periodic Table of elements

3. Different morphologies of MTMOs

The morphologies of MTMOs include tetragonal or hexagonal nanosheets, nanorods, microspheres, nanoplatelets, and spherical nanoparticles. MTMOs have a variety of oxidation states, making them excellent electrode materials. Electrical conductivity and the specific surface area for the faradaic redox reaction are improved by hybridising MTMOs with graphene **[25].** By including oxalic acid, porous $NiCo_2O_4$/NiO/Co_3O_4 nanoflowers were synthesized with improved specific capacitance, power densities and energy densities **[26]**. 3D Co_3O_4@NiO organized nanowire arrays showed a specific capacitance useful for supercapacitors **[27].** Molybdenum sulphide (MoS_2) blended with reduced graphene oxide (rGO) on 3D nickel foam showed improved performance over the bare MoS_2 electrode was synthesised using layer-by-layer (LBL), followed by solution-based ionic layer adsorption and reaction (SILAR) showed substantial improvement in capacitance **[28].**

There are numerous possible uses for the $NiCo_2O_4$ microspheres as supercapacitor electrode materials **[29]**. Hybridization of MTMO with graphene nanosheets has garnered a lot of scientific interest because of the special intrinsic properties of graphene, which enhance electrical conductivity and increase the specific surface area of the nanocomposite for Faradaic redox reaction **[30]**. Through direct nanoparticle nucleation and growth on nitrogen doped, rGO sheets and cation substitution of spinel Co_3O_4 nanoparticles, a spinel structure of $MnCo_2O_4$@graphene hybrid electrode was demonstrated as a highly effective electrocatalyst for the O_2 reduction reaction in alkaline conditions **[31]**. 2D holey MTMO nanosheets composed of connected MTMO nanocrystals are produced using reduced graphene oxide (rGO) templates (**Fig 2**) **[32]**.

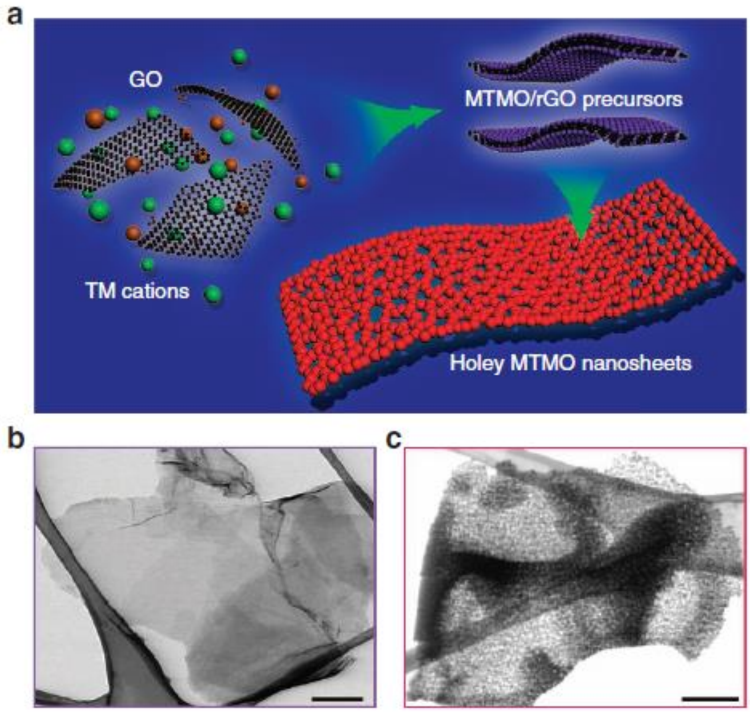
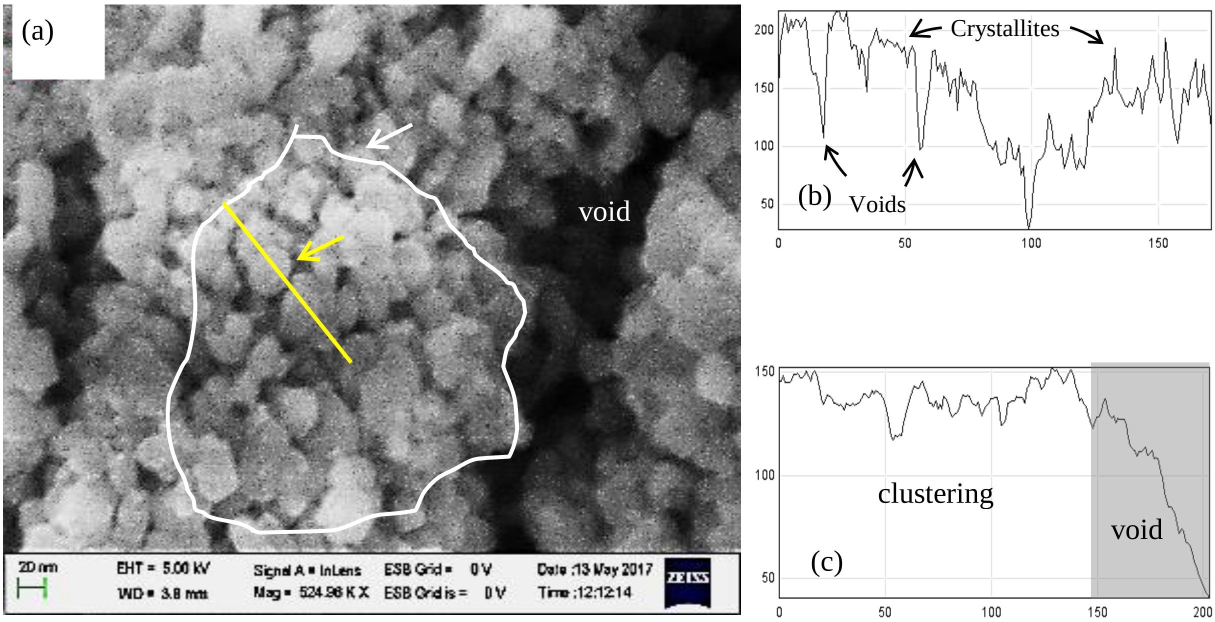


Fig 2. – **Reproduced from Peng, L., Xiong, *et al.* Holey two-dimensional transition metal oxide nanosheets for efficient energy storage. *Nat Commun* 8, 15139 (2017). under CC -BY License** [32] (a) Holey mixed transitional meatal oxide nano sheets synthesis by with the help Graphene Oxide and Transitional Metal Cations. (b) STEM image of ZMO precursor/rGO shows sheets-like morphology. (c) STEM image of 2D holey ZMO nanosheets shows holey nanosheets composed of interconnected ZMO nanocrystals. Scale bars, 200nm (b, c)

4. $ZnMn_2O_4$ (ZMO) and ZMO/rGO

Sol-gel thermolysis was used to create $ZnMn_2O_4$ (ZMO) nano powder. The $ZnMn_2O_4$ nano powder was found to have a pure phase and tetragonal structure with 20 nm crystallite size. The materials showed impressive specific capacity. ZMO nanoparticles got coagulated with some porosity (**Fig3**) **[33].** The porous nature obtained from combustion synthesis of was advantageous for electrolytic mobility and showed a larger discharge capacity than ZMO due to graphene's increased conductivity. The CV tests of ZMO/rGO also had a greater specific capacitance than ZMO substitute. [34].



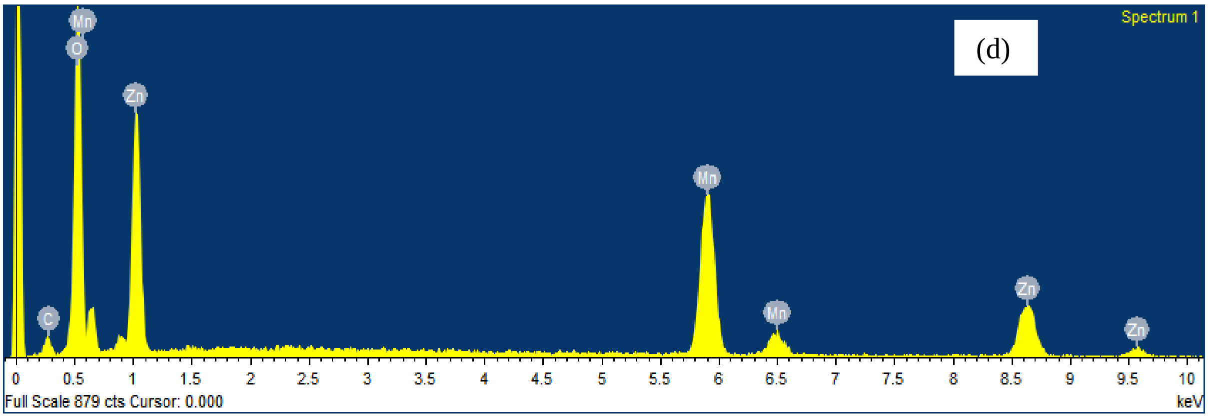


Fig 3. (a) FE-SEM images of $ZnMn_2O_4$ at (c) lower magnification, d) higher magnification. (e) EDAX analysis of ZMO Elemental analysis (f) Cyclic Voltammetry of ZMO and (g) Cyclic numbers of ZMO. **Reproduces with with permission from Elsevier [33]**

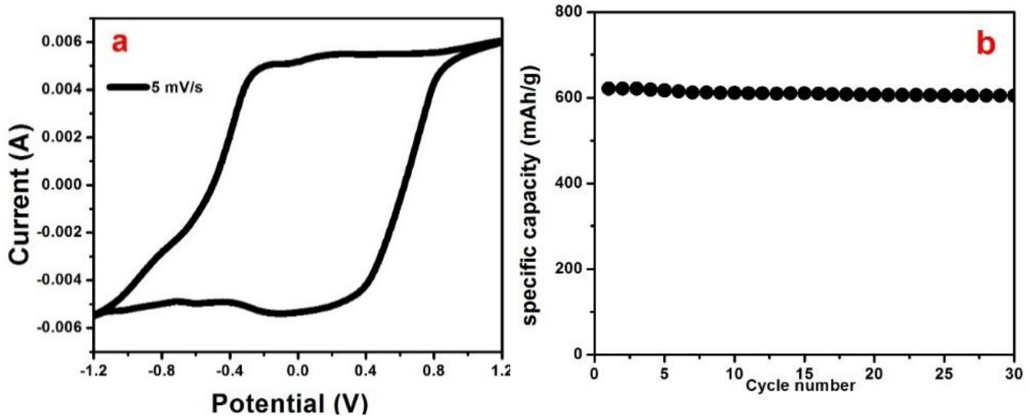


Fig 3. (a) Cyclic Voltammetry of ZMO and (b) Cyclic numbers of ZMO. **Reproduces with with permission from Elsevier [33]**

Reference

1. Asit Sahoo, Yogesh Sharma, Synthesis and characterization of nanostructured ternary zinc manganese oxide as novel supercapacitor material, Materials Chemistry and Physics, 149-150 721-727 (2015).
2. Hongbin Chen, Liang-Xin Ding, Kang Xiao, Sheng Dai, Suqing Wang, Haihui Wang, Highly ordered ZnMnO3 nanotube arrays from a self-sacrificial ZnO template as high-performance electrodes for lithium-ion batteries, J. Mater. Chem. A., 4, 16318–16323 (2016).
3. Yanping Gao, Mingbo Zheng, Huan Pang, Achieving High-Performance Supercapacitors by Constructing Porous Zinc–Manganese Oxide Microstructures, Energy Technol., 3, 820 – 824 (2015).
4. Rahul R. Salunkhe, Yusuf V. Kaneti, Yusuke Yamauchi, Metal–Organic Framework-Derived Nanoporous Metal Oxides toward Supercapacitor Applications Progress and Prospects, ACS Nano., 11 5293–5308 (2017).
5. Rahul R. Salunkhe, Jing Tang,Yuichiro Kamachi, Teruyuki Nakato, Jung Ho Kim, Yusuke Yamauchi, "Asymmetric Supercapacitors Using 3D Nanoporous Carbon and Cobalt Oxide Electrodes Synthesized from a Single Metal–Organic Framework", ACS Nano., 9, 6288–6296 (2015).
6. Rahul R.Salunkhe, Jianjian Lin, Victor Malgras, Shi Xue Dou, Jung Ho Kim, Yusuke Yamauchi, "Large-scale synthesis of coaxial carbon nanotube/Ni $(OH)_2$ composites for asymmetric supercapacitor application, Nano Energy, 11, 211-218 (2015).
7. Tong Zhang, Yu Gao, Huijuan Yue, Hailong Qiu, Zhendong Guo, Yingjin Wei, Chunzhong Wang, Gang Chen, Dong Zhang, "Convenient and high-yielding strategy for preparing nano-ZnMn2O4 as anode material in lithium-ion batteries", Electrochimica Acta.,198 84–90 (2016).
8. Lei Luo, Hui Qiao, Ke Chen, Yaqian Fei, Qufu Wei, Fabrication of electrospun $ZnMn_2$O4 nanofibers as anode material for lithium-ion batteries", Electrochimica Acta., 177, 283–289 (2015).
9. Wei Hau Low, Poi Sim Khiew, Siew Shee Lim, Chiu Wee Siong, Ejikeme Raphael Ezeigwe, Recent development of mixed transition metal oxide and graphene/mixed transition metal oxide-based hybrid nanostructures for advanced supercapacitors, J. Alloys and Compds, 775, 2019, Pages 1324-1356,
10. J.M. Tarascon, M. Armand, "Issues and challenges facing rechargeable lithium batteries", Nature., 414, 359 (2013)
11. L.F. Xiao, Y.Y. Yang, J. Yin, Q. Li, L.Z. Zhang, "Low temperature synthesis of Flowerlike $ZnMn_2O_4$ superstructures with enhanced electrochemical lithium storage", Journal of Power Sources., 194, 1089 (2009).
12. J. Zhu, G. Zhang, X. Yu, Q. Li, B. Lu and Z. Xu, Graphene double protection strategy to improve the SnO_2 electrode performance anodes for lithium-ion batteries. Nano Energy., 3, 80–87 (2014).

13. H. Wang, L. F. Cui, Y. Yang, H. S. Casalongue, J. T. Robinson, Y. Liang, Y. Cui and H. Dai, "Mn_3O_4 graphene hybrid as a high-capacity anode material for lithium ion batteries." J. Am. Chem. Soc., 132, 13978–13980 (2010).
14. L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng and X. W. Lou, "Formation of Fe2O3 microboxes with hierarchical shell structures from metal-organic frameworks and their lithium storage properties." J. Am. Chem. Soc., 134, 17388–17391 (2012).
15. H. Song, L. Shen and C. Wang, Template-free method towards quadrate Co3O4 nanoboxes from cobalt coordination polymer nano-solids for high performance lithium-ion battery anodes" J. Mater. Chem. A., 2, 20597–20604 (2014).
16. Huang XH, Xia XH, Yuan YF, Zhou F, "Porous ZnO nanosheets grown on copper substrates as anodes for lithium-ion batteries. Electrochem Acta., 56:4960–5(2011).
17. Du, N. Xu, Y. F. Zhang, H. Yu, J. X. Zhai, C. X. Yang, D. R, "Porous ZnCo2O4Nanowires Synthesis via Sacrificial Templates: High- Performance Anode Materials of Li-ion Batteries." Inorg. Chem., 50, 3320−3324 (2011).
18. Liu, J.; Liu, C. Wan, Y. Liu, W. Ma, Z. Ji, S. Wang, J. Zhou,Y. Hodgson, P. Li, Y, "Facile Synthesis of NiCo2O4Nanorod Arrays on Cu Conductive Substrates as Superior Anode Materials for High-Rate Li-Ion Batteries." Cryst Eng. Comm., 15, 1578−1585 (2013).
19. G. Zhang, L. Yu, H.B. Wu, H.E. Hoster, X.W. Lou, "Formation of ZnMn2O4 ball-in ball hollow microspheres as a high-performance anode for lithium-ion batteries", Advanced materials., 24 4609–4613 (2012).
20. Indra Mohan, Anshu Raj, Kumar Shubham, D.B. Lata, Sandip Mandal, Sachin Kumar, Potential of potassium and sodium-ion batteries as the future of energy storage: Recent progress in anodic materials, Journal of Energy Storage, 55, B, 2022 105625
21. Bhimanaboina Ramulu, S. Chandra Sekhar, Shaik Junied Arbaz, Manchi Nagaraju, Jae Su Yu,Nickel–cobalt phosphate nanoparticle-layer shielded in-situ grown copper–nickel molybdate nanosheets for electrochemical energy storage, *Energy Storage Materials*, 44,379-389 (2022)
22. Sivalingam Ramesh, K. Karuppasamy, Dhanasekaran Vikraman, P. Santhoshkumar, Chinna Bathula, Ramasubba Reddy Palem, A. Kathalingam, Hyun-Seok Kim, Joo-Hyung Kim, Heung Soo Kim, Sheet-like morphology CuCo2O4 bimetallic nanoparticles adorned on graphene oxide composites for symmetrical energy storage applications, *Journal of Alloys and Compounds*,892, 162182(2022)
23. N. Rahmatian, A. Bo, K. Randhir, J.F. Klausner, J. Petrasch, Bench-scale demonstration of thermochemical energy storage using the Magnesium-Manganese-Oxide redox system, Journal of Energy Storage, 45, 103682. (2022)
24. T. Kavinkumar, N. Naresh, Georgeena Mathew, B. Neppolian, Urchin-like porous NiCo2O4 nanostructure: Morphology control using porous reduced graphene oxide nanosheets for high performance flexible transparent energy storage devices, Journal of Alloys and Compounds, Volume 891, 2022,162052 (2022)
25. Bulakhe, R.N., Bhalerao, A.B., In, I. (2021). Mixed Transition Metal Oxides for Energy Applications. In: Ezema, F.I., Lokhande, C.D., Jose, R. (eds) Chemically Deposited Nanocrystalline Metal Oxide Thin Films. Springer, Cham.
26. Xuansheng Feng, Ying Huang, Chao Li, Xuefang Chen, Suhua Zhou, Xiaogang Gao, Chen Chen, Controllable synthesis of porous NiCo2O4/NiO/Co3O4 nanoflowers for asymmetric all-solid-state supercapacitors, Chemical Engineering Journal, Volume 368, 2019, Pages 51-60, ISSN 1385-8947,
27. Qingqing Hu, Zhengxiang Gu, Xiaoting Zheng, Xiaojun Zhang, Three-dimensional Co3O4@NiO hierarchical nanowire arrays for solid-state symmetric supercapacitor with enhanced electrochemical performances, Chemical Engineering Journal, Volume 304, 2016, Pages 223-231,
28. Ravindra N. Bulakhe, Van Hoa Nguyen, Jae-Jin Shim Layer-structured nanohybrid MoS2@rGO on 3D nickel foam for high performance energy storage applications. New J. Chem., 2017,**41**, 1473-1482
29. Weiqian Zhang, Wangpeng Xin, Tingting Hu, Qinghua Gong, Tingting Gao, Guowei Zhou, One-step synthesis of NiCo2O4 nanorods and firework-shaped microspheres formed with necklace-like structure for supercapacitor materials, Ceramics International, Volume 45, Issue 7, Part A, 2019, Pages 8406-8413, ISSN 0272-8842

30. Yuan, C., Wu, H.B., Xie, Y. and Lou, X.W. (2014), Mixed Transition-Metal Oxides: Design, Synthesis, and Energy-Related Applications. *Angew. Chem. Int*. **2014** Ed., 53: 1488-1504.
31. Liang, Y. et al. Covalent hybrid of spinel manganese–cobalt oxide and graphene as advanced oxygen reduction electrocatalysts. *J. Am. Chem. Soc.* **2012**, 134, 3517–3523.
32. Peng, L., Xiong, P., Ma, L. *et al.* Holey two-dimensional transition metal oxide nanosheets for efficient energy storage. *Nat Commun* 2017, **8**, 15139.
33. Parameshwar Kommu, G P Singh, A S Bhattacharyya Sol gel thermolysis process for the synthesis of nano $ZnMn_2O_4$ by using PVA with combustion fuel and their electrochemical properties *J. Energy Storage* 2018, 16, 156-159.
34. Parameshwar Kommu, G P Singh, A.S. Bhattacharyya Preparation of $ZnMn_2O_4$ and $ZnMn_2O_4$/graphene nano composites by combustion synthesis for their electrochemical properties, *Materials Science & Engineering B* (261) **2020**, 261, 114647.