

Pristine and Doped Transition Metal oxides for Lithium Ion Batteries

A S Bhattacharyya^{1,2} and P Kommu¹

¹Centre of Excellence in Green and Efficient Energy Technology (CoE GEET)

²Central University of Jharkhand

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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-shell, nanorods, nanosheets etc and in the forms of composites with materials like PANI, rGO, CNT, CNF etc

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P.Komu¹, A. S. Bhattacharyya^{1,2*}

Department of Metallurgical and Materials Engineering¹
Centre of Excellence in Green and Efficient Energy Technology (CoE GEET)²
Central University of Jharkhand, Brambe, Ranchi: 835205

*Email: arnab.bhattacharya@cuja.ac.in, 2006asb@gmail.com

Abstract

Mixed transition metal oxides with adjustable composition and structures are widely used in electrochemical 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-shell, 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 NiCo₂O₄/rGO on Ni foam gives more active sites with high energy density. The porous carbon network acts as nucleation sites for Nanorod network of NiCo₂O₄/Au which are used as flexible/transparent supercapacitors with good energy density along with power density [21-24].

										5	6	7	8
										B	C	N	O
										13	14	15	16
										Al	Si	P	S
22	23	24	25	26	27	28	29	30	31	32	33	34	
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
40	41	42	43	44	45	46	47	48	49	50	51	52	
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	

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 NiCo₂O₄/NiO/Co₃O₄ nanoflowers were synthesized with improved specific capacitance, power densities and energy densities [26]. 3D Co₃O₄@NiO organized nanowire arrays showed a specific capacitance useful for supercapacitors [27]. Molybdenum sulphide (MoS₂) blended with reduced graphene oxide (rGO) on 3D nickel foam showed improved performance over the bare MoS₂ 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 NiCo₂O₄ 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 Co₃O₄ nanoparticles, a spinel structure of MnCo₂O₄@graphene hybrid electrode was demonstrated as a highly effective electrocatalyst for the O₂ 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].

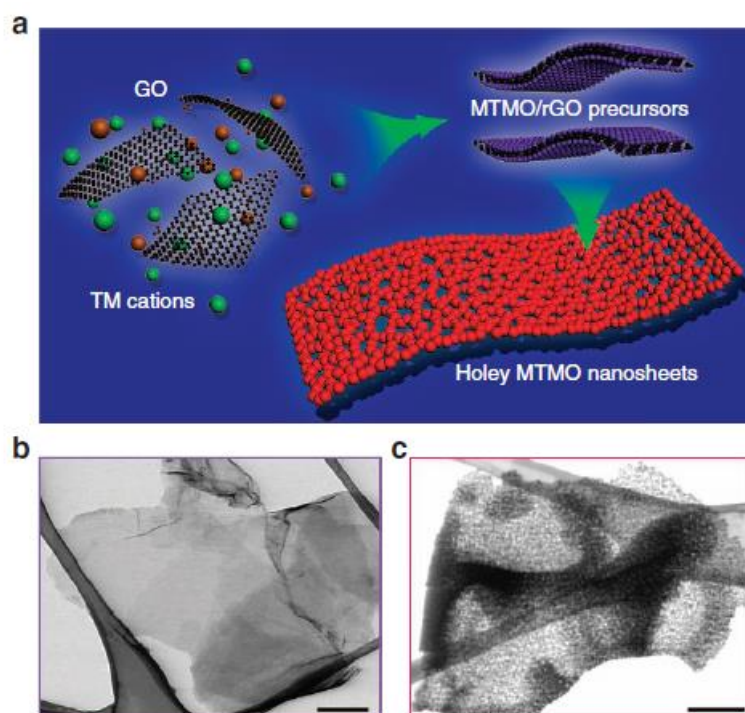


Fig 2. – Reproduced from Peng, L., Xiong, *et al.* Holey two-dimensional transition metal oxide nanosheets for efficient energy storage. *Nat Commun* 8, 15139 (2017). under CC -BY License [32] (a) Holey mixed transitional metal oxide nano sheets synthesis by with the help Graphene Oxide and Transitional 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].

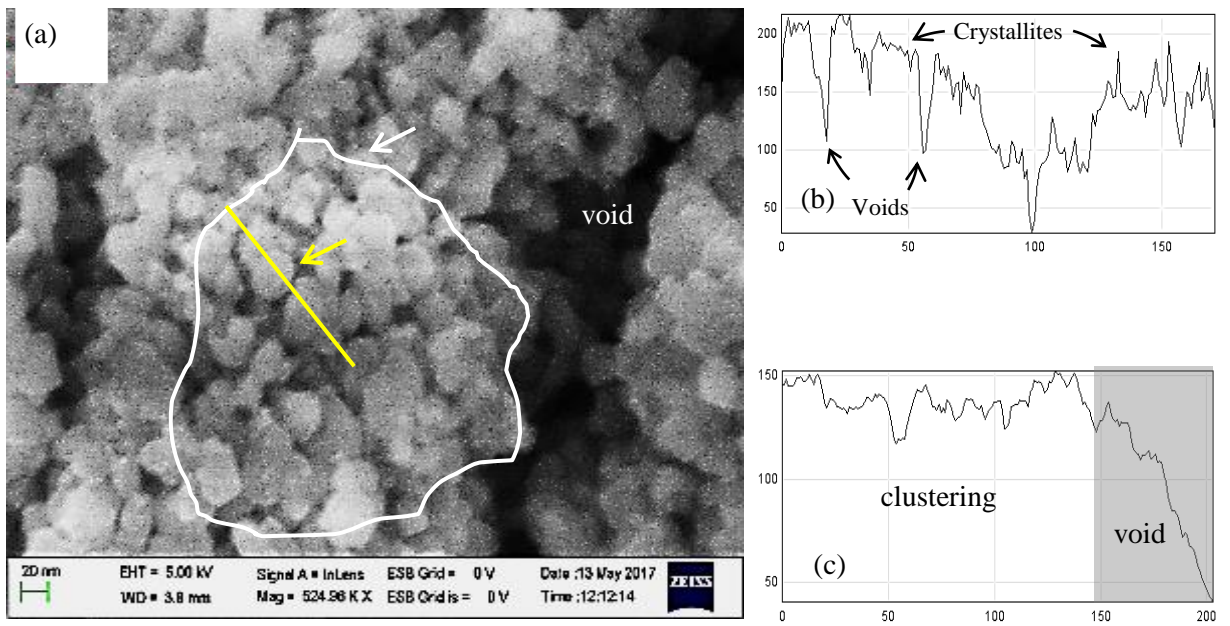


Fig 3. (a) FE-SEM images of ZnMn₂O₄ at (c) lower magnification, (d) higher magnification. (e) EDAX analysis of ZMO Elemental analysis (f) Cyclic Voltammety of ZMO and (g) Cyclic numbers of ZMO. **Reproduces with with permission from Elsevier [33]**

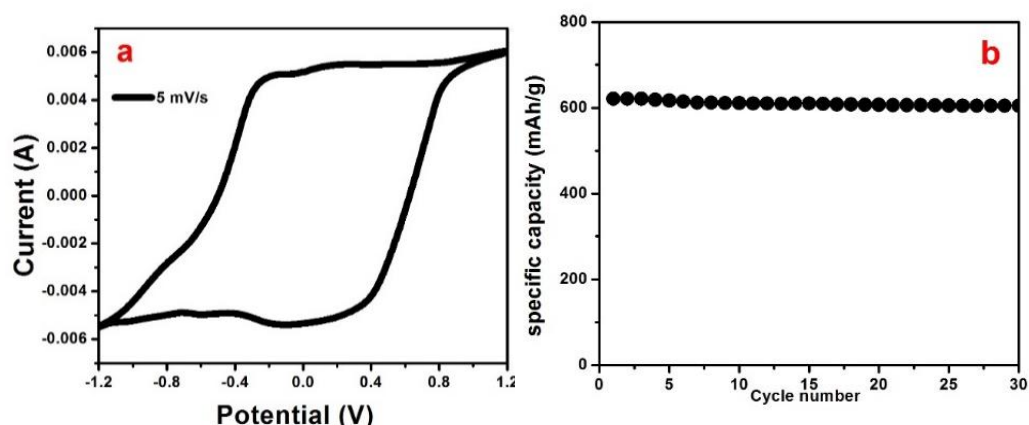


Fig 3. (a) Cyclic Voltammetry of ZMO and (b) Cyclic numbers of ZMO. Reproduces with permission from Elsevier [33]

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