

**Fabrication of High-Performance Perovskite Oxide
Based Hybrid Supercapacitors for energy storage
applications**

BY

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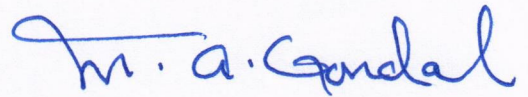
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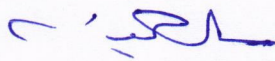
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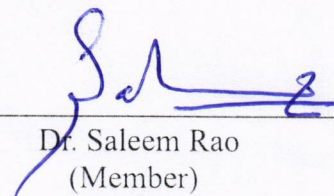
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Fabrication of High-Performance Perovskite Oxide Based Hybrid Supercapacitors for energy storage applications

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Dedication

“I DEDICATE MY THESIS TO MY FAMILY AND TEACHERS”

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In the name of **ALLAH**, the most gracious and most merciful.

First of all, I want to thank **ALLAH** almighty who gives me the courage and strength to avail the opportunity to study at one of the most prestigious universities in the world.

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ABSTRACT

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The growing need for fast-charge, high-capacity energy storage solutions has led to the development of new materials in supercapacitor research. This MS thesis focused on fabrication and characterization of Perovskite oxide-based electrode materials for high-performance hybrid supercapacitors. Herein we synthesized four novel electrode materials Mn-Ru co-doped LaNiO_3 , $\text{La}_2\text{MnFeO}_6$, $\text{La}_2\text{MnCoO}_6$, and $\text{La}_2\text{MnFeO}_6/\text{TiC-MXene}$ nanocomposite using advanced material synthesis techniques. The synthesized nanomaterials were then analyzed by using advanced characterization techniques i.e. XRD, XPS, SEM, FTIR, and TGA) to elucidate their structural, chemical & electronic, morphological, and thermal properties. Their electrochemical performances were tested through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) to evaluate their suitability for hybrid supercapacitors. The findings reveal remarkable redox activity, significant specific capacitance, as well as improved energy and power density, particularly in $\text{La}_2\text{MnFeO}_6/\text{TiC-MXene}$ nanocomposite due to the synergistic effects and favorable electronic structure. Detailed discussions provide insights into the correlation of materials, structural properties, and electrochemical performance, which contributes to designing higher-performing energy storage devices.

Keywords: supercapacitor (SC), supercapacitors (SCs), asymmetric supercapacitors (ASCs), Hybrid supercapacitors (HSCs), specific capacitance (C_{sp}), power density (P_d), energy density (E_d), electric double layer capacitors (EDLCs), activated carbons (ACs), transition metal oxides

(TMOs), conducting polymers (CPs), potential window (PW), perovskite oxides (POs)

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أدت الحاجة المتزايدة لحلول تخزين الطاقة سريعة الشحن وعالية السعة إلى تطوير مواد جديدة في أبحاث المكثفات الفائقة. تصنيع وتوصيف أطروحة الماجستير هذه لمواد القطب الكهربائي المعتمدة على أكسيد البيروفسكايت للمكثفات الفائقة الهجينة عالية ، ومركب $\text{La}_2\text{MnCoO}_6$ ، و $\text{La}_2\text{MnFeO}_6$ ، و LaNiO_3 ، Mn-Ru الأداء. قمنا هنا بتصنيع أربع مواد إلكترونيات جديدة من باستخدام تقنيات تصنيع المواد المتقدمة. تم بعد ذلك تحليل المواد النانوية المصنعة $\text{La}_2\text{MnFeO}_6/\text{TiC-MXene}$ نانوي ، (XPS)، التحليل الطيفي للأشعة السينية الضوئية (XRD) باستخدام تقنيات التوصيف المتقدمة مثل حيود الأشعة السينية ، (FTIR)، التحليل الطيفي للأشعة تحت الحمراء لتحويل فورييه (FESEM) المجهر الإلكتروني لمسح الانبعاثات الميدانية لتوضيح خصائصها الهيكلية والكيميائية والإلكترونية والمورفولوجية (TGA) وقياس الوزن الحراري الحراري. تحليل ، ومطياف (GCD)، وتفرغ الشحنة الجلفانية (CV) والحرارية. تم اختبار أدائها الكهروكيميائي من خلال قياس الجهد الدوري لتقييم مدى ملاءمتها للمكثفات الفائقة الهجينة. تكشف النتائج عن نشاط الأكسدة والاختزال (EIS) المعاوقة الكهروكيميائية $\text{La}_2\text{MnFeO}_6/\text{TiC-MXene}$ الملحوظ، والسعة المحددة الكبيرة، بالإضافة إلى تحسين الطاقة وكثافة الطاقة، خاصة في مركب النانوي بسبب التأثيرات التآزرية والبنية الإلكترونية الملائمة. توفر المناقشات التفصيلية رؤى حول العلاقة بين المواد MXene والخصائص الهيكلية والأداء الكهروكيميائي، مما يساهم في تصميم أجهزة تخزين الطاقة ذات الأداء العالي.

CHAPTER 1

INTRODUCTION

1.1 Background

Many researchers are exploring different renewable and green energy harvesting sources, i.e., solar, wind, heat, etc. for the generation of electricity. But the major problem with these renewable energy harvesting sources is that they provide intermittent energy supplies and do not deliver all the time as per demand. To address this challenge, one requires energy storage devices that can store energy and provide a constant output when required. To achieve such objectives, Supercapacitors (SCs) are gaining great attention from material scientists [1]. Batteries and supercapacitors are two well-known energy storage devices. Batteries have low power density (P_d) and low life cycles [2]. Due to chemical reactions, it is very difficult to use them for some applications that require fast charging and discharging. On the other hand, supercapacitors (SCs) have high P_d ($\geq 10 \text{ KWkg}^{-1}$), long life cycle ($\geq 10^5$ cycles), and wide operating temperature range [3].

Among energy storage devices, Li-ion batteries are promising candidates for energy storage with high energy density and energy storage efficiency, but it has some serious disadvantages like limited Li resources, unequal Li distribution throughout the earth, and safety problems due to their toxicity make Li-ion batteries non-promising candidate in long run for energy storage application [4]. So, Supercapacitors are becoming an alternative to conventional batteries as a means of storing energy and filling the gap between energy and power density of traditional capacitors (high P_d) and batteries (high E_d) [5] shown in Figure 1. Energy storage devices called supercapacitors

(SCs), sometimes referred to as ultracapacitors, have received a lot of interest recently because of their fast charging and discharging times, and long cycle life [6]. Such devices can be used in a variety of fields, including hybrid cars, regenerative braking systems, grid energy storage, and portable electronics. These devices have the potential to revolutionize many areas of energy storage, from transportation to renewable energy systems [7]. One main issue that restricts supercapacitors for industrial applications is low energy density and high cost [8]. In this work, we present high-performance perovskite oxide-based electrode materials for supercapacitors (to deliver high E_d).

Figure 1 presents a Ragone plot showing the energy and power density ranges of various electrochemical devices.

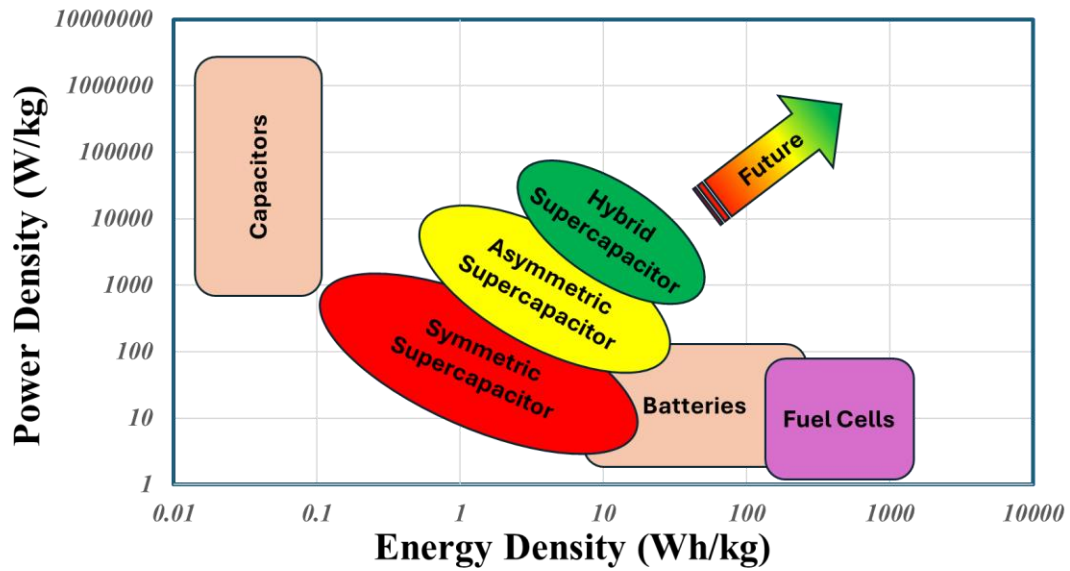


Figure 1. Ragone Plot

1.2 Types of Supercapacitors

Based on the charge storage mechanism, SCs can be categorized into three main categories. These are electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors

(HSCs) shown in Figure 2. EDLCs generally involve the adsorption of charges at the electrode/electrolyte boundary through a non-faradic process. While pseudo capacitors store charges through faradic processes. HSCs are a combination of EDLC and pseudocapacitors.

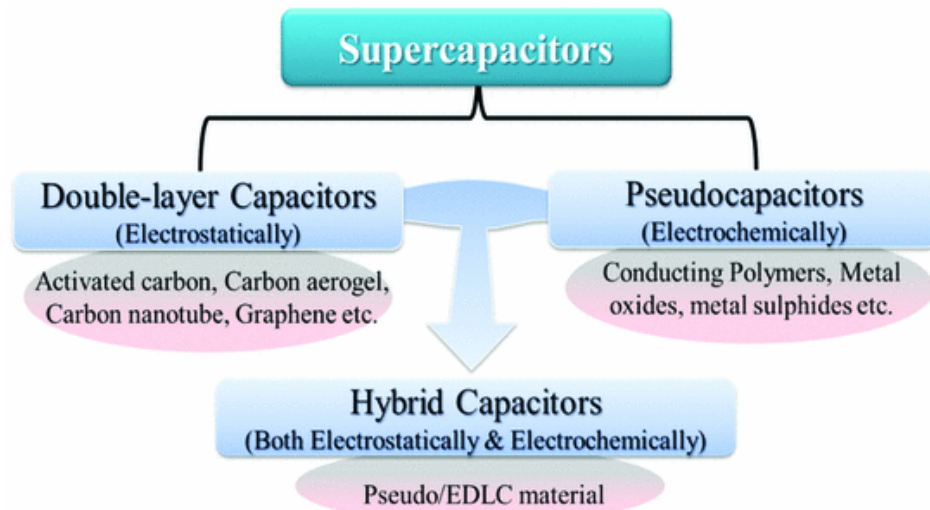


Figure 2. Types of supercapacitors

EDLC functions by adsorbing and desorbing of the electrolyte ions, creating a double layer in the boundary of the electrode and the electrolyte. In contrast, pseudocapacitors utilize reversible redox reactions between electrolyte & electrode material for charge storage, which is why they are also referred to as faradaic supercapacitors. Hybrid supercapacitors, on the other hand, employ both the EDLC and pseudocapacitor mechanisms to store energy [9]. As a result, hybrid supercapacitors possess a significant advantage in that they combine the favorable characteristics of both EDLC and pseudocapacitors. This leads to a high specific capacitance, E_d , and P_d [10]. Supercapacitors can be classified into two categories based on their fabrication method: symmetric and asymmetric supercapacitors. Symmetric supercapacitors consist of two identical electrodes (positive and negative), while asymmetric supercapacitors are made up of two dissimilar electrodes [11, 12]. Supercapacitors offer numerous benefits. Nonetheless, further research is

necessary to enhance their performance and decrease the high cost of widespread application. The type of electrode materials used plays a significant role in improving the performance of supercapacitors and reducing their cost [13].

Traditional electrode materials primarily consist of carbon materials, conductive polymers, and hydroxides [14]. To the best of our knowledge, the use of these electrode materials is limited due to existing structural and performance deficiencies [15]. The commonly utilized electrode materials for energy storage are carbon materials, but they demonstrate low specific capacitance due to the restricted charge transfer at the electrode/electrolyte interface, particularly in electrical double-layer capacitors (EDLCs) [16]. As pseudocapacitive materials, transition metal oxides are used to explore advanced electrode materials with excellent performance to overcome the limitations of traditional materials [17]. The performance of electrode materials is primarily governed by their structure, and therefore, enhancing the structure becomes the primary avenue to improve their performance. Perovskite oxides generally exhibit high structural and thermal stability with high electrical conductivity, which are key features that make them highly desirable materials for various applications, including energy storage [18]. Consequently, perovskites prove to be an outstanding choice as electrode materials for energy storage purposes.

Moussa et al., have studied conducting polymer (CPs) hydrogels synthesized by a novel approach that led to increased electronic conductivity and large surface area and then used for supercapacitors but found short cycling life [19]. Sassin et al. also studied conducting polymers and found a short cycling life for supercapacitor applications [20]. Additionally, some of the transition metal oxides were also studied for SC applications and found them be cost-effective and practical SC electrode materials, but they have low energy density which restricts them from use as SC electrode materials [21-23]. Due to the high surface area of some pure carbon materials i.e., carbon nanotubes, activated carbons, and graphene, they are tested for SCs applications [24]. Then

some perovskite oxide-based materials were studied by different groups and found that, in comparison to the above-discussed materials, perovskite oxides have long cycling life, high charge storage capacity, and stable structure [25, 26] And, can be used for SC applications, if we achieve high energy density.

There is an important formula for the tolerance factor that defines the stability of ABO_3 -type crystal structures [27]. It can be written as $t = (\sqrt{R_A} + \sqrt{R_O}) / (\sqrt{R_B} + \sqrt{R_O})$, Here t is the tolerance factor, R_A is the ionic radius of the A-site atom, R_B is the atomic radius of the B-site atom & R_O is the atomic radii of the O-atom. Generally, the value of “ t ” between 0.8 to 1 is considered a mechanically stable structure [28]. because it reflects a geometric balance which allows the corner octahedral network of unit cell to form without considerable distortion.

1.3. Aim and Objective

The main objectives of the thesis are;

1. To explore single (ABO_3), double($A_2B_2O_6$), and perovskite oxide nanocomposites for high-performance HSCs.
2. To synthesize high-performance, non-toxic, environment-friendly, and cost-effective perovskite oxide-based electrode materials.
3. To look at new perovskite oxides/other material (MOs, MXenes, CPs, ACs, etc.) composites, design approaches, and manufacturing techniques that could be used to enhance the performance of supercapacitors while keeping the cost down.
4. To characterize the synthesized materials using advanced characterization techniques i.e. XRD, XPS, SEM, EDS, BET, TEM, and TGA.

5. To evaluate the fabricated supercapacitor devices using electrochemical analysis techniques i.e. cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), electrochemical Impedance analysis (EIS), and the stability of the SCs devices.

CHAPTER 2

LITERATURE REVIEW

Perovskite materials have the chemical formula ABX_3 , where A is generally Lanthanide or Alkaline earth metal, and X is oxygen (for perovskite oxides). They are a new class of materials having some excellent properties such as high electron mobility, high ionic conductivity, high thermal stability, and faradic redox reactions [29, 30]. Perovskite oxides are categorized as single POs, double POs, triple POs, and their derivatives. Single perovskite oxides have formula ABO_3 , Double perovskite oxides are represented by $AA'BB'O_6$, and triple perovskite oxides can be represented by $AA'A''BB'B''O_9$ [31]. In perovskites, A and B-sites essentially influence thermodynamical stability and electrochemical reaction respectively [32]. So, chemical substitution on the A-site and B-site can alter the properties. The first lanthanum-based POs used in SCs was $LaMnO_3$. $LaMnO_3$ exhibits a stable and constant oxygen excess [33].

2.1 The single perovskite oxides

Because of its oxygen vacancy concentration and high power density, ABO_3 exhibits great potential as an active electrode material for SCs. There are four types of perovskite oxides: cerium-based, strontium-based, lanthanum-based, and other POs.

2.1.1. Lanthanum-based POs.

For single perovskites, mostly La-based perovskites e.g., LaCoO₃, LaNiO₃, LaFeO₃, etc. have been explored in recent years [34-36] due to the facile synthesis, high thermal stability, low-cost, oxygen vacancies, and better electrical conductivity [37]. Among these LaNiO₃ showed the highest specific capacitance 719 F g⁻¹ in neutral electrolytes [38]. The first lanthanum-based POs used in SCs was LaMnO₃. LaMnO₃ exhibits a stable and constant oxygen excess [33]. Mefford et al. reported a C_{sp} of approximately 609.9 F g⁻¹ for LaMnO₃ in 2014 [39]. LaMnO₃ and LaNiO₃ have been reported to have similar charge storage mechanisms, however, LaNiO₃ has less electrical resistivity (roughly 10⁻⁴ ohm) [40, 41]. LaFeO₃ is more stable than LaNiO₃ [42]. Hussain's group synthesized a hierarchical mesoporous LaCrO₃ nanostructure using the cost-effective sol-gel synthesis method. The prepared material showed great stability (91.4% retention at 5000.0 cycles) [43].

2.1.2. Strontium-based perovskite oxides

As SC electrode materials, strontium-based perovskite oxides have garnered a lot of research interest due to their natural abundance, strong electronic & ionic conductivity, and resistance to reduction, oxidation cycling [44]. It was in 1999 that strontium-based POs were first used in the field of SCs [45]. SrRuO₃ was reported by Garche et al.[46] to have a capacitance of 270 F g⁻¹. The orthorhombic structure of SrCoO_{2.5} was synthesized via a traditional solid-state reaction process, and the final product showed a specific capacitance of 168.5 F g⁻¹ [47]. The charge storage capabilities of mesoporous SrTiO₃ having cubic crystal structure were shown by Sharma et al. [48] The average pore diameter and volume of SrTiO₃ measured in the Barrett-Joyner-Halenda (BJH) study were 15.18 nm and 0.249 cm³, respectively. These pores offer low charge transfer resistance and a high number of active sites.71 As a result, at 5 mV s⁻¹, STO showed a high capacitance of 592 F g⁻¹. Remarkably, an SC with exceptional cycling stability of (99% capacitor retention after 5000 cycles), a maximum energy density of (27.8 W h kg⁻¹) and P_d of (1921 W kg⁻¹

¹) was generated using this material.

2.1.3. Cerium-based perovskite oxides.

The high bandgap, low cost, variable valence states between Ce^{3+} and Ce^{4+} , and high dielectric constant of cerium-based perovskite oxides make them appealing candidates [49]. Recently, it was discovered that the specific capacitance of cerium-based perovskite oxides (CeCoO_3 , CeNiO_3 , and CeCuO_3) was 128, 189, and 117 F g^{-1} , respectively [50].

2.1.4. Other perovskite oxides

Other single perovskite oxides (like BiFeO_3 , NiMnO_3 , NiTiO_3 , and CoTiO_3) have also drawn attention recently in addition to the several types already covered [51-54]. A lot of research has also been done on the metal titanate MTiO_3 ($\text{M} = \text{Ni, Co}$) as a SC material. Mesoporous nickel rods were synthesized using the sol-gel technique in Kitchamsetti's work [53]. An excellent C_{sp} of (542.260 F g^{-1}) was demonstrated by the obtained sample. Similarly, Kochamsetti et al. [54] reported on highly porous CoTiO_3 microrods that had high E_d (9.77 W h kg^{-1}), and C_{sp} (608.4 F g^{-1}).

2.2. Doped Perovskites

The electrochemical performance of a supercapacitor mainly depends on the choice of electrode materials, along with other factors. Perovskite materials with the general formula ABO_3 are considered favorable for supercapacitor electrode materials. Generally, the A-site contains lanthanides (i.e., La, Nd, Sr, Gd, Y, Ce, etc.) [55]. Meanwhile, the B-site consists of transition metals (i.e., Ni, Fe, Mn, Co, Zn, etc.) [56]. These perovskite structures also possess many exciting features, such as good ionic conductivity, suitable redox behavior, and good electrical conductivity [57].

Among the nanosized transition metal oxides (TMOs), NiO appears to have a much higher theoretical C_{sp} value [58]. Varying oxidation states, non-toxic, low cost, and natural abundance make it attractive for energy storage applications [58]. NiO is a strong candidate for supercapacitor

use due to its impressive morphological and physiochemical properties. Perovskite oxides have been widely studied for decades due to their exceptional redox behavior, including LaNiO_3 [59, 60], LaMnO_3 , and LaFeO_3 [61-63]. Some researchers reported that based on perovskite (LaNiO_3) hollow spheres have a specific capacitance of 422 Fg^{-1} at a current density of 1 Ag^{-1} with good cyclic stability [34]. Some explored La-based perovskites (LaCrO_3 , LaMnO_3 , LaNiO_3 , LaFeO_3) and found that LaNiO_3 has the highest C_{sp} of 106 Fg^{-1} with 98% cyclic retention after 5000 cycles @ 1 Ag^{-1} [64]. The composite of LaNiO_3 with doping of Sr has a honeycomb-like structure and exhibited a capacity of 115.88 mAhg^{-1} @ 0.6 Ag^{-1} with a cyclic retention of 104.4% after 16000 cycles [65]. $\text{LaNiO}_3/\text{NiO}$ has a specific capacitance of 326.8 Fg^{-1} and cyclic retention of 97.7% after 3000 cycles [66]. LaNiO_3 perovskite nanofiber doped with Sr exhibits a C_{sp} of 719 Fg^{-1} with excellent cyclic stability [38]. LaNiO_3 can be used as electrode material in supercapacitors because Ni has several valence states that allow redox reactions. LaNiO_3 nanocomposite was also reported for electrochemical supercapacitor applications [67-69]. Several reports describe the co-doped LaNiO_3 like Mn and Mn-Nd, which have been extensively studied in magnetic, optical, and catalytic behaviors for supercapacitor applications [70-72].

The abovementioned literature shows that La-based doped perovskite materials can be used as electrode material for supercapacitors, and minute doping can enhance electrochemical performance. Despite reports showing the advantages of perovskite (LaNiO_3) doped materials, it still have limitations as their low electronic conductivity significantly inhibits practical applications for energy storage. Thus, the LaNiO_3 should be co-doped by substituent hetero atoms to improve electrochemical performance further. In this scenario, herein, we report the first time Mn-Ru co-doped LaNiO_3 perovskites using a low-cost sol-gel method and studied the excellent electrochemical properties. The variable oxidation states of Mn and Ru significantly improve the specific capacity of electrode material, thereby enhancing electrochemical performance.

Perovskites' structural stability helps provide a high E_d and P_d . In addition, the formation of extra oxygen vacancies inside the co-doped perovskite oxide framework enables efficient ionic intercalation/deintercalation, which is responsible for improved electrochemical kinetics. We develop a series with the general formula $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.00, y=0.00$), ($x=0.02, y=0.08$), ($x=0.05, y=0.05$), ($x=0.08, y=0.02$) with the main objective of achieving high C_{sp} , E_d & P_d for high-performance supercapacitor applications. The performance of the optimized $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ -based two-electrode asymmetric device validates it as a promising energy storage system.

2.3. Double perovskite oxides

Perovskite oxides are categorized as single POs, double POs, triple POs, and their derivatives. Single perovskite oxides have $\text{AA}'\text{BB}'\text{O}_6$, and triple perovskite represent formula ABO_3 ; double perovskite oxides can be represented by $\text{AA}'\text{A}''\text{BB}'\text{B}''\text{O}_9$ [31]. In perovskites, A and B-sites influence thermodynamical stability and electrochemical reaction, respectively [32]. So, chemical substitution on the A-site and B-site can alter the properties.

Steward and Rooksby made the first discovery of double perovskite oxides in 1951. The crystal structure of single perovskite oxides can be destroyed due to leaching of cation in aqueous electrolyte [4, 73]. Fortunately, we found double and triple perovskites with more stable crystal structures [74]. Additionally, there are broader potential windows (PW) for them due to which we get high E_d by the relation $E=1/2 \text{ CV}^2$. Substitution of A or B-site elements can turn single POs (ABO_3) into double POs ($\text{A}_2\text{BB}'\text{O}_6$). Some studied double perovskite oxides for SCs are $\text{La}_2\text{CoMnO}_6$, $\text{Ba}_2\text{Bi}_{0.1}\text{Sc}_{0.2}\text{Co}_{1.7}\text{O}_6$, and $\text{Sr}_2\text{CoMoO}_6$ [75-77]. Several studies discussed the potential or practical use of double POs ($\text{AA}'\text{BB}'\text{O}_6$) as the electrode material for the SC [76-78]. The surface area can also be modified in addition to the internal modifying of double POs. The formation of an ordered structure is the major internal modification of POs for use in SCs.

Following the substitution of various metal ions, double perovskite $\text{Ba}_2\text{Bi}_{0.1}\text{Sc}_{0.2}\text{Co}_{1.7}\text{O}_{6-\delta}$ exhibiting ordered B-site cations demonstrated a stable crystal structure compared to BSCF, measuring 1.47 times higher [75]. The electrochemical performance of R_2MMnO_6 ($\text{R} = \text{Gd, La; M} = \text{Ni, Zn, Cu}$) POs, such as $\text{La}_2\text{ZnMnO}_6$, $\text{La}_2\text{CuMnO}_6$, and $\text{Gd}_2\text{NiMnO}_6$, was reported by Kumar's team [79-81]. These perovskite oxides demonstrated C_{sp} of 718.6 F g^{-1} , 205.5 F g^{-1} , and 400.46 F g^{-1} , respectively, at various current densities. One method used for producing Y_2NiMnO_6 nanowires (NWs) was hydrothermal. The resulting Y_2NiMnO_6 NWs showed a specific capacitance of (77.76 F g^{-1}) that was greater than that of the equivalents made using the sol-gel technique [2].

Increasing the number of oxygen vacancies is a useful tactic to improve capacitance because they can serve as charge-storage sites. The amount of oxygen vacancies in perovskite oxides is largely influenced by their composition and structure. Perovskite oxides with a good design are therefore essential to obtaining good electrode performance. Wang et al. [82] used the sol-gel method to create the A-site cation-ordered double POs, $\text{PrBaCo}_2\text{O}_5$ (PBCO). They discovered that the Pr^{3+} planes' oxygen atoms can be partially or completely removed, resulting in a large number of oxygen vacancies in the POs structure.

Additionally, the properties of composite materials are typically better than those of their constituent parts. PBCO demonstrated a notable superiority in cyclic stability (93.0% capacitance retention at 10.0 Ag^{-1}) compared to certain single POs, including BiFeO_3 and LaMnO_3 [83, 84]. As B site elements, research has been done on Mn, Fe, Ni, and Co. It has been demonstrated that adding a metal element to the B-site can effectively produce oxygen vacancies in POs, improving their performance as SC electrodes [85, 86]. The energy-storage performance of perovskite oxides is further enhanced by electrolytes. The most studied media are by far aqueous electrolytes, such as Na_2SO_4 (2 V) and KOH, which have limited working voltage ranges of 1.23 V and 2.0 V,

respectively. The energy density can be further increased by using organic (2.50–3.50 V) or ionic liquid electrolytes (1.5–6 V), which provide a broad potential window (PW).

The electronic, magnetic, and photonic features of $\text{La}_2\text{MnCoO}_6$ (LMCO) and $\text{La}_2\text{MnFeO}_6$ (LMFO) have already been studied elsewhere, but the comparative electrochemical properties of LMCO and LMFO as supercapacitor electrodes have not yet been investigated. Herein, we present extraordinary La_2MnXO_6 (X=Co, Fe) double perovskite as an SC electrode material. Sol-gel technique was applied to prepare $\text{La}_2\text{MnCoO}_6$ (LMCO) and $\text{La}_2\text{MnFeO}_6$ (LMFO) nanorods. The lattice constants of LMCO and LMFO were determined using XRD analysis. The existence of evenly distributed nanorods was established using scanning electron microscopy. Using Tauc's plot, the bandgap for $\text{La}_2\text{MnCoO}_6$ and $\text{La}_2\text{MnFeO}_6$ was estimated. A relatively high specific capacitance value was attained using 1M KOH electrolyte. The CV curve's asymmetric form demonstrated redox processes indicating battery-type supercapacitors' behavior. Furthermore, the proportion contribution of capacitance and diffusion behavior was also calculated using Dunn's approach.

2.4. Transition metal oxides/MXene nanocomposites

For the last 10 years, much work has been directed towards high-performance electrode materials derived from two-dimensional (2D) materials because of their high surface area, 2D arrangement characteristics, flexibility, and great mechanical properties. Graphene [87, 88] was the first 2D material that enabled others to find different members in the 2D materials family. The current family of 2D materials includes semimetals (graphene), hexagonal boron nitride (hBN), semiconducting transition metal dichalcogenides (TMDCs), highly conductive MXenes, black phosphorus (BP), germanene, and silicon[89].

Among the mentioned 2D materials, MXenes (transition metal nitrides, carbides, and carbonitrides) have attracted extensive research interest due to their high specific surface area,

conductivity, and hydrophilicity [90-92]. This gives MXene its uniqueness among other 2D materials. However, there remain some problems that haven't been addressed such as low capacitance, unreacted microstructure, poor surface functional groups, and restacking despite the great performance of MXene's. However, several approaches have been employed to mitigate the aforementioned challenges including doping, morphology manipulation, and their composites with different materials i.e. TMOs for improving energy storage devices performance [93-95]. Among above-mentioned strategies, the composite of MXene with other materials is the most feasible option to enhance their performance. These electrochemical properties include pseudocapacitance and redox behavior, and TMOs such as WO₃, MnO_x, NiO, MoO₃, V₂O₅, & even TiO₂ are normally applied to these purposes [96-101]. As a result, their favorable electrochemical performances make the composites of MXenes with TMOs form synergistic structures and become an attractive strategy for energy storage devices [102]. In addition, MXene/TMO composites have high ionic conductivity and good long-term cycling stability for balanced charge storage, enabling potential application as a high-performance electrode for energy storage devices. The fast intercalation enabled by greater interplanar distance in MXene layers is responsible for facilitating charge storage performance and C_{sp} without sacrificing cyclability and P_d . However restacking & aggregation of MXene layers reduce active site interaction with the electrolyte [103, 104]. Although bare MXenes possess good electrochemical properties, there are still some hurdles as they tend to aggregate/ restack because of the Van der Waals (vdW) interactions and hydrogen bonding among MXene layers [105, 106]. This limits MXene to act as an electrode in energy storage devices. One of the simplest methods to overcome the aforementioned limitation of MXene is through combination with other materials like polymer [107], carbon [108], and TMOs-based materials [102]. Compared with carbon materials & polymers, the composite of TMOs with MXenes may reduce the volume expansion problems of

TMOs and limit the restacking problem of MXene nanosheets, which can give rise to improved electrochemical properties for the MXene/TMO mixed architectures.

Manganese oxide (MnO_2) is a pseudocapacitive supercapacitor electrode material with a high theoretical specific capacitance of 1370 F g^{-1} [109], But, its low conductivity inhibits its potential use. The lowest conductivity of MnO_2 is typically improved through combination with highly-conductive materials, including new nano-materials such as 2D MXene nanosheets. In particular, different $\text{MnO}_2/\text{MXene}$ nanocomposite configurations including nanowires, nanodots, nanoneedles, and even nanosheets have been studied in recent years that introduce enhanced performance to supercapacitors. Beside MnO_2 , Many other TMOs like Fe_2O_3 , Co_3O_4 , NiO & Fe_3O_4 [101, 110-112] has shown superb electrochemical behavior. Although these electrode materials show the high theoretical C_{sp} that results from their Faradaic redox reactions of metal cations but they have poor conductivity & a very short cyclic stability. In order to overcome these limitations, it has been suggested that when combined with superb conductive MXenes, the aforementioned TMOs material for SCs can be enhanced in terms of electrochemical properties.

In this thesis, A combined 2D Ti_3C_2 -MXene and $\text{La}_2\text{MnFeO}_6$ perovskite oxide hierarchical composite electrode material has also been studied for supercapacitor applications. Owing to their high electrical conductivity, hydrophilic nature and tunable surface chemistry of MXenes are an ideal platform for energy storage. With great structural flexibility and redox activity, perovskite oxides are plentiful in active sites for faradaic reactions which can greatly augment the energy storage ability with low restacking properties. Here, the composite made up of 2D Ti_3C_2 -MXene and $\text{La}_2\text{MnFeO}_6$ perovskite combines their advantages to get remarkable electrochemical performance. This unique design integrates high conductive MXenes with robust redox-active perovskites, producing a new class of materials possessing simultaneously high C_{sp} , and excellent cycling stability. With this research, we hope to overcome the current drawbacks of supercapacitor

materials and help in developing energy storage technology that is both efficient as well as sustainable.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), Ruthenium nitrate ($\text{Ru}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Nickle Nitrate ($\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Iron Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), anhydrous ethanol, MAX phase (Ti_3AlC_2), Hydrofluoric Acid (HF) and citric acid were used as initial precursors. All were bought from Sigma-Aldrich Co., Ltd. The chemicals were employed as received.

3.2. Synthesis of un-doped and Mn-Ru Co-doped LaNiO_3 perovskites:

$\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ having the ratio of ($x = 0, y = 0$), ($x = 0.02, y = 0.08$), ($x = 0.05, y = 0.05$) and ($x = 0.08, y = 0.02$) were prepared by using the sol-gel synthesis technique using above mentioned raw materials. To synthesize, a specific amount of lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), ruthenium nitrate, nickel nitrate, and 3g of citric acid were dissolved in 30 ml of deionized water. The mixture was then placed on a magnetic stirrer at 90°C until a clear solution is formed (with no precipitates). Once we got a clear solution, a small amount (2ml) of ethylene glycol was added. Following that, ammonia solution was added to the Sol to adjust the pH to 7 to prevent any kind of possible precipitations. Once pH was adjusted, the

temperature of the stirrer was increased to 100 °C. At this temperature, water evaporated, and the formation of gel started. The gel burnt at 200 °C and converted into fluffy powder and grind to get a fine powder. Then the obtained powder was calcinated at 800 °C for 12 hours to get the final desired product. The same procedure was employed for the preparation of all desired ratios of Mn-Ru co-doped LaNiO_3 . The schematics of the preparation steps are presented in **Figure. 3**

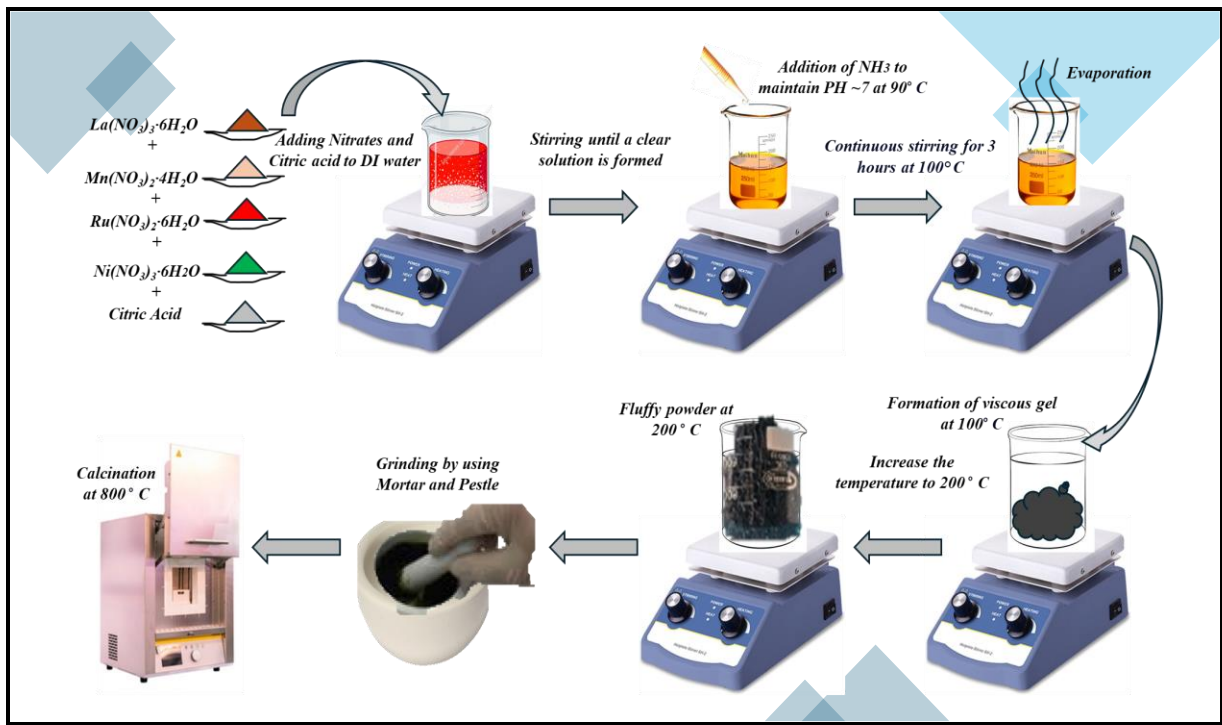


Figure 3. Synthesis of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$ using Sol-gel method

3.3. Synthesis of LMCO and LMFO double perovskite

LMCO and LMFO nanorods were prepared using the sol-gel synthesis technique and the above-mentioned raw materials. To synthesize LMCO, a specific amount of Lanthanum nitrate, manganese nitrate, and cobalt nitrate at a molar ratio of 0.02:0.01:0.01 mole and 3g of citric acid in 30 ml of deionized water. The mixed solution is then placed on a stirrer at 80 °C until a clear solution is formed (With no precipitates). Once we got a clear solution, a small amount (2ml) of ethylene glycol was added. An ammonia solution was added to the Sol to adjust the pH to 8 and

prevent any possible precipitation. After adjusting the PH, the stirrer was heated to 250 °C. At this temperature, water evaporated, and the development of gel started. The gel was burnt at this temperature and ground to get a fine powder. Then, the obtained powder was calcinated at 800 °C for 12 hours to get the final desired crystalline structure/product. The same procedure was employed for the preparation of LMFO nanorods. The schematics of the preparation steps are presented in Figure 4.

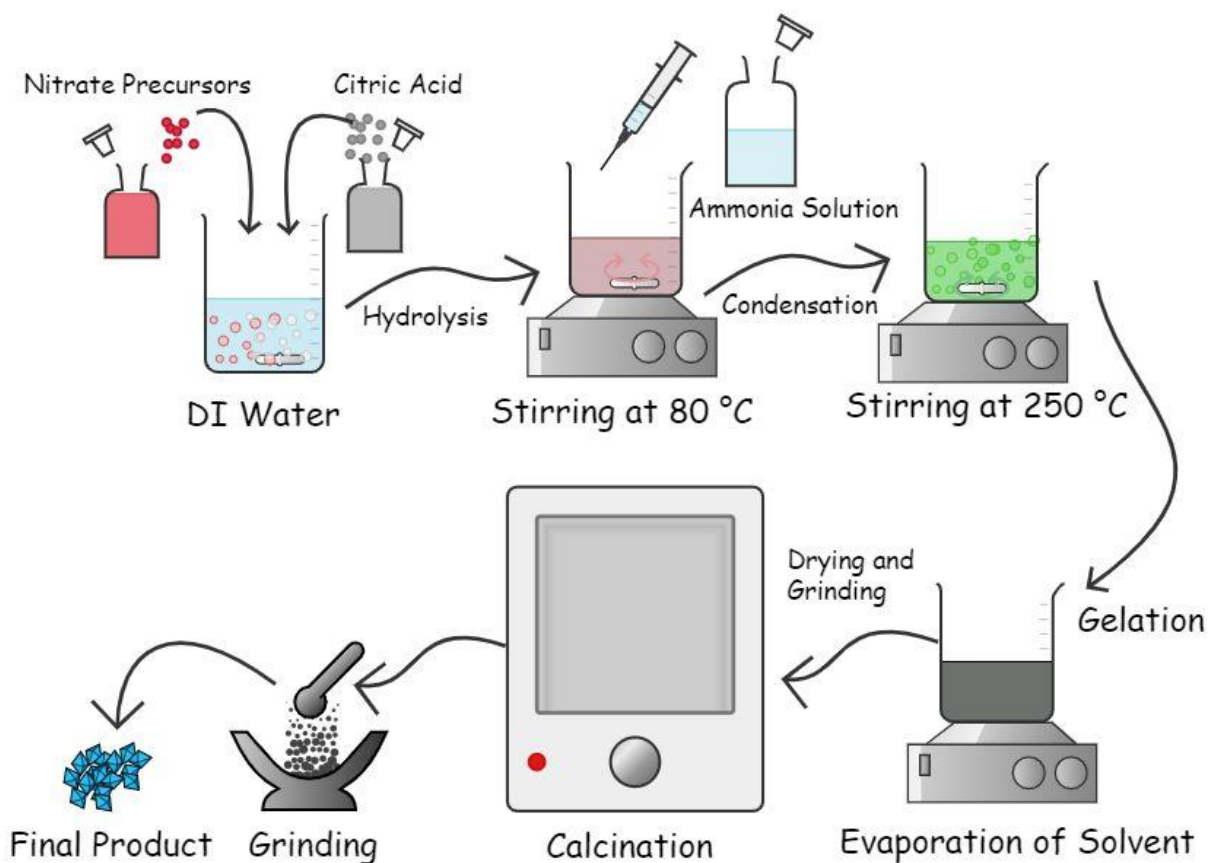


Figure 4. Synthesis of LMCO and LMFO nanorods

3.4. Synthesis of 2D $\text{Ti}_3\text{C}_2\text{-MXene}$:

The Ti_3C_2 MXene was synthesized by chemical etching of the Ti_3AlC_2 MAX phase, in HF. Ti_3AlC_2 powder was gradually added into a solution (40% HF and 60% DI water) and stirred continuously to allow for an equal reaction throughout the solution. The etching was kept at 60° C for the next 48 h, resulting in the

selective removal of aluminum (Al) layers and thus the formation of a layered Ti_3C_2 structure. The obtained product was washed with DI water by repeating until the PH became neutral. In order to obtain the delaminated MXene nanosheets, the Ti_3C_2 slurry was subjected to deionized water and then high-speed centrifugal separation at a centrifuge speed of around 4,000 rpm multiple times, which separated the single- or few-layered MXene sheets. Dried, delaminated MXene was collected and thoroughly characterized for supercapacitor application. The schematic of the preparation steps are presented in Figure 5.

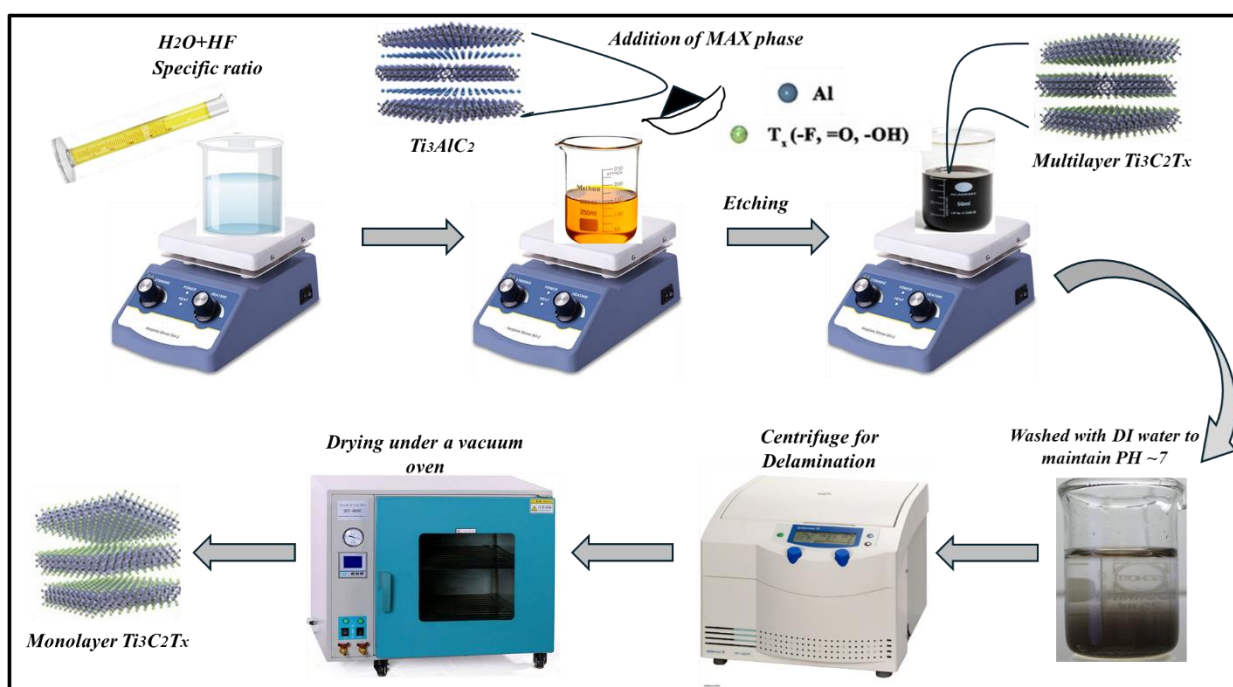


Figure 5. Synthesis of Ti_3C_2 MXene

3.5. Composite synthesis:

The ultrasonication method was used to prepare the nanocomposite (Figure 6.). First of all, the precursors (Ti_3C_2 -Mxene & $\text{La}_2\text{MnFeO}_6$) were thoroughly dissolved in DI water using stirring at 60 °C for 30 min. Then the mixture was ultrasonicated at room temperature for 60 minutes to ensure well mixing and dispersion of the ingredients. This suspension was sonicated and then filtered through filter paper. The collected material was subsequently dried in an oven at 60 °C until fully dry. The final mixture was collected and stored for further characterization and analysis.

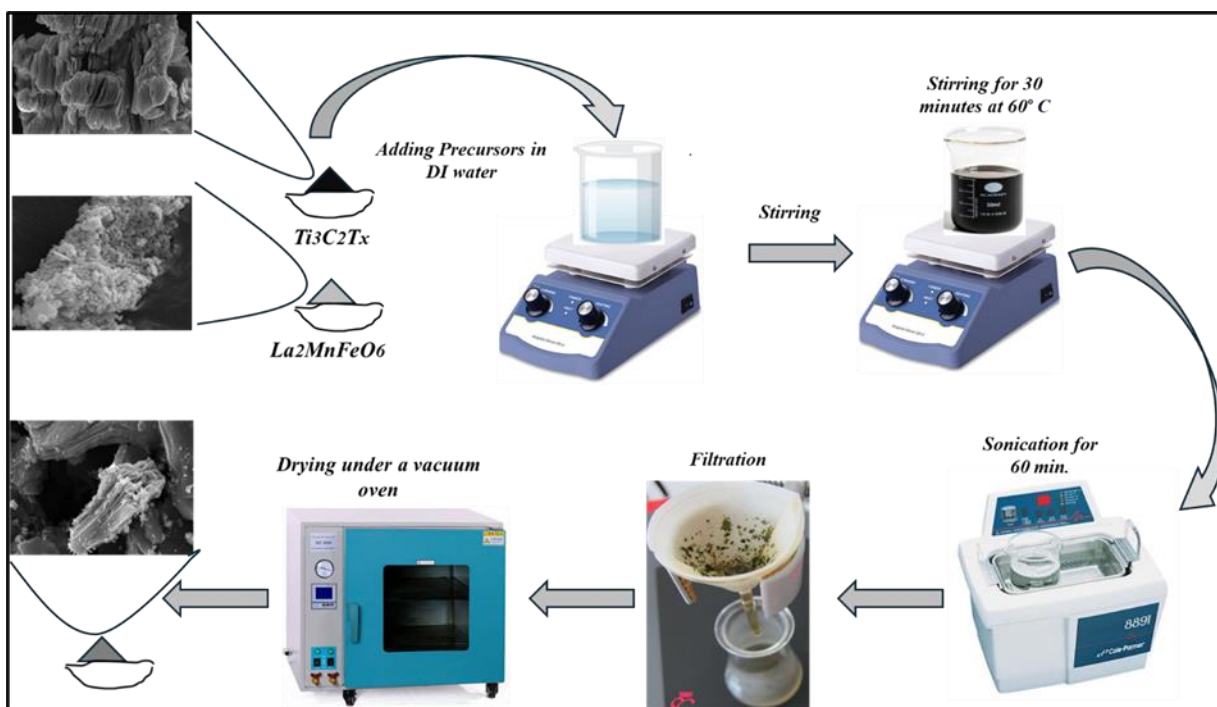


Figure 6. Synthesis steps of $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite

3.6. Characterizations

To get the crystal structure information, X-ray diffraction testing was used. XRD (Bruker, $\text{Cu K}\alpha$, $\lambda = 1.5406 \text{ \AA}$) between the 2-theta range of $10^\circ\text{-}90^\circ$ @ ~ 2 degrees per min. were used for the analysis of the samples. The surface morphology was investigated using Field Emission SEM (FE-SEM). The ultraviolet-visible (UV-vis) diffuse reflectance spectra of were measured employing a Shimadzu UV-3600i plus UV-vis spectrophotometer. FTIR was used for the functional group analysis. Thermal analysis was investigated using TGA/DTA analysis in an N_2 gas environment. For the surface electronic and chemical states analysis, XPS was employed.

3.6.1. X-ray Diffraction (XRD):

X-rays are the part of electromagnetic radiation spectrum which lies between ultra-violet and γ -rays region. Its wavelength is shorter than the ultra-violet rays and longer than the γ -rays. Its

wavelength values vary from 0.01-10 nm. And its energy varies from 100 eV-100 keV. In year 1885 x-rays were discovered by a scientist from Germany named Wilhelm Rontgen. While working in lab on effect of the cathode rays, Rontgen discovered the x-rays, on that time the nature of these rays is unknown so that is why the name given to this electromagnetic radiation is x-rays. These rays are sometimes often called Rontgen radiation on the name of the scientist who discovered them. There are two types of x-rays one is hard x-rays and second is soft x-rays. The photonic energy values of hard x-rays are much higher than that of soft x-rays. Hard x-rays have 5 to 10 keV values which can penetrate objects deeply as compared to soft x-rays [113]. Due to this ability of deeply analysis given by the hard x-rays; it gives us the inner information of the objects. Accordance to its application point of view hard x-rays is used in wide variety of the application such as in hospitals for medical radiography, and for security purpose.

The wavelength of the hard x-rays is equivalent to the size of atom or smaller, so that is why hard x-rays are used to investigate the crystal structure information of the materials such as d-spacing, lattice parameters and Bragg's angle. Soft x-rays have long wavelength and low energy as compared with hard x-rays, they also cannot penetrate through any object, and it can be easily absorbed in air.

XRD is a non-damaging technique, and it can be used to determine lattice parameters and to find the crystalline structure. In X-ray diffraction, X-ray beams are dispersed when they interact with the sample material. Due to constructive interference, these X-ray beams support each other. This whole process is known as X-ray diffraction. XRD defines the structural pattern of the crystal of sample material and gives us much information about the internal arrangement of atoms in a crystal.

Basic Principle:

When an X-ray beam is targeted on a crystal of sample material which strikes the atoms, it forces electrons to vibrate. The electrons oscillate with the same frequency as the incident X-ray beam. In this process, at some positions, constructive interference will occur due to the consistent alignment of atoms. Contrary to this some positions will show destructive interference [114]. The constructive interference is due to the combination of rays in-phase and destructive interference is due to the combination of rays out of phase.

For the determination of crystal structure and the phase analysis powder x-ray diffraction (XRD) method was used mostly. In powder x-ray diffraction, to produce x-rays a beam of electron bombards at Copper (Cu) target, when these rays strike with target material, they emit some x-rays with different intensities from copper materials or the targeted material. The intensity of these x-rays changes with wavelengths depending on the nature of the targeted material. A single crystal of Ge can be used to produce a monochromatic beam of x-rays. On the polycrystalline targeted sample a monochromatic beam of x-rays falls, these samples are made up of different arbitrarily oriented grains having different dimension ranges from 1-500 μm . When x-rays strike the targeted material they hit the atoms of that material, and then scattered at different angles. These diffracted angles depend upon the nature of the material such as atomic position of that material, after diffracted from atoms these scattered x-rays hit the detector at a different angle position. In 1915, Paul Scherer and Peter Debye (Dutch and Swiss physicists) were the first who used a photographic film to get data of the different position of the diffracted x-rays by enclosing the sample. These photographic films act as a detector which contains the series of lines which represents the diffracted angle (2θ), and the intensity (I).

According to Bragg's law, constructive interference is will occur only if the reflected rays are in phase.

$$2d_{hkl}\sin\theta = n\lambda \quad (a)$$

Where order of reflection is represented by $n = 0,1,2, \dots$, and d is the inter-planer spacing.

Equation (a) can be rearranged,

$$\frac{n\lambda}{2d_{hkl}} = \sin\theta < 1 \quad (b)$$

$2d_{hkl}$ must be greater than $n\lambda$ because θ less than 1.

For diffraction occurrence at any angle, we have one condition.

$$\lambda < 2d_{hkl}$$

$n = 1$ is the minimum value for the occurrence of diffraction. For a simple cubic structure, the relation between “ d ” inter-planer spacing, “ hkl ” miller indices and “ a ” lattice parameter is:

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (c)$$

For diffraction there are some conditions that need to be filled, firstly it will satisfy the Bragg’s law conditions otherwise the diffraction phenomena of x-rays is not possible. We assume that crystals of all possible orientations exist when using powder samples and that the strength varies with angle based on atomic distribution within each plane. To achieve a significant diffraction sample, it is important to emphasize that sufficient preparation of fine powder in powder XRD is essential.

Applications of XRD

XRD is a non-destructive technique, some of the uses of XRD are:

- Finding of arrangement of atoms by X-ray diffraction.
- Differentiation between amorphous and crystalline materials.
- Determination of the structure of crystalline material.
- Determination of the single crystal orientation.
- Determination of poly-grained material texture.
- Determination of crystallite size.
- Determination of X-ray density.
- Separation distance between two layers can be determined.

Studies show that X-ray diffraction (XRD) is an important technique for characterizing the crystal structure of perovskite oxides in supercapacitor research. It is used to confirm the crystal structure of ABO_3 and determine crystallinity, impurities, or secondary phases. The XRD technique is also

utilized for understanding the effect of doping as a shift in peak positions occurs due to incoming dopant atoms with different sizes and hence reveals an effect on lattice parameters. This structural knowledge is crucial for fine-tuning the electrochemical performances when aiming at more stable perovskite-based supercapacitors.

3.6.2. Fourier-transform Infrared Spectroscopy (FTIR):

FTIR (Fourier Transform Infrared) spectroscopy relies on the fact that molecules will absorb certain infrared (IR) frequencies that will make their bonds vibrate. This technique identifies the various molecular structures and functional groups by looking at the absorbed frequencies and resulting spectrum. Fourier Transform Infrared Spectroscopy (FTIR) Fourier transform infrared spectroscopy is a crucial tool for studying chemical bonds and functional groups within materials. Key information regarding the chemical bonds found in the POs and their nanocomposites were analyzed via FTIR analysis. In supercapacitor research, FTIR is essential for distinguishing the chemical nature of bonds and confirming whether certain groups exist (e.g., identifying metal-oxygen bonds which are important in demonstrating redox activity & stability).

3.6.3. Thermogravimetric Analysis (TGA):

Thermogravimetric Analysis (TGA) Determination measures changes in weight of a substance due to heat exposure and is used to analyze physical and chemical processes that lead to weight loss. This enabling the study of phase transitions. Knowing the temperature ranges at which POs and their composites perform well without degradation or mass loss requires TGA/thermal stability analysis. When assessing their prospective as electrode materials for supercapacitors that can operate across a wide temperature range, this type of information is essential. Furthermore, the TGA data will tell the suitable temperature ranges for the device.

3.6.4. X-ray Photoelectron Spectroscopy (XPS) Analysis:

XPS can determine a surface elemental composition in addition to the chemical and electronic states of its atoms [115]. X-ray Photoelectron Spectroscopy (XPS) is an important surface analytical technique to obtain the surface chemistry and electronic structure of perovskite oxide electrode materials. XPS offers an in-depth analysis of the surface atoms, covering their elemental identity, oxidation states, and chemical bonding (for example oxygen vacancy effects; nature of surface interacting species). X-ray photoelectron spectroscopy (XPS) is particularly critical for the characterization of perovskite oxide. It tells about oxidation states of transition metals (Mn, Fe, Co, or Ru), which directly influence their redox activity and thus electrochemical performance.

3.6.5. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) Mapping:

The working principle of SEM is based upon the interaction of accelerated electrons with the sample surface [116]. In SEM analysis, the powdered samples are typically used. An electron beam is incident on the sample surface and produces secondary electrons, X-ray's photons and back-scattered electrons which are collected by the detector [117]. These electrons are then transmitted in the form of signals to the screen which creates a two-dimensional image of the surface. An electron beam interaction with the surface of the sample gives us all the information about sample surface morphology & compositions (using EDX).

Scanning electron microscope is made up of two main magnets i.e., scanning magnet and focusing magnet that works on Lorentz forces. It is used to regulate the spot diameter of the beam by making it to focus on a specific spot and shows that beam diameter which is as minimum as 1nm changes by changing the amount of current through coil spots. It also consists of an electron gun, a detector, and the sample stage. Electron Gun releases electrons by thermionic emission of the cathode [117]. These electrons are accelerated with an electric field to achieve maximum energy which is usually 30 keV. Generally, image data by SEM depends upon the production of SE or BSE. As these SE

originated from shallow surface areas, so SEM with a secondary electron detector can only create the image of surface topology. The images formed by SEM contain brighter spots which indicate the presence of heavier elements in the material's composition (using EDX) [118].

Energy-dispersive X-ray's spectroscopy (EDX) refers to an analytical technique for the determination of elemental or chemical compositional analysis of the required sample. The EDX analysis is used to find out the elemental configuration of individual points or to map out the adjacent distribution of elements from the specific imaged area and is not a technique for the morphological studies of the materials

We often use Scanning Electron Microscopy (SEM) for surface morphology and particle size characterization. SEM images can provide information on how the distribution of particles, surface roughness, and porosity affect electrochemical performance. In the case of perovskite oxides, SEM can clearly reveal changes in morphology due to synthesis methods and doping such as increased porosity which improves ion diffusion. The surface morphology of the POs and their composite was investigated using SEM imaging. EDS mapping, in conjunction with SEM.

3.6.6. Electrochemical measurements:

A variety of electrochemical techniques (CV, GCD, and EIS) were employed to assess the electrochemical properties of the electrode materials after they have been synthesized and characterized. Cyclic Voltammetry (CV) quantifies the electrochemical properties of a material by sweeping the potential of the system and measuring the resultant current response, generating information about the redox reactions that occur as well as the kinetics of reaction and charge storage. The Galvanostatic Charge-Discharge (GCD) test is performed to evaluate the energy storage capacity along with cycling performance by applying constant current for charging and discharging which gives the data for specific capacitance and energy density. EIS or Electrochemical Impedance Spectroscopy records the behavior of impedance across a spectrum

of frequencies to observe charge transfer resistance and ion diffusion in energy storage devices.

The obtained as-synthesized $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$, LMCO, LMFO, and $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite was combined with binder and conductive carbon in a weight ratio of 80:10:10 to make the working electrode. A few drops of Solvent (NMP) made the mixture slurry. This slurry solution was coated uniformly on the Ni foam and baked for 12 hours at 90 °C to obtain working electrodes.

They were initially investigated through a three-electrode system containing a working electrode (active material coated on Ni foam), a counter electrode (platinum wire), and a reference electrode (Ag–AgCl) correspondingly using 1M KOH as an electrolyte. [119]. The full devices were then fabricated by using the optimized ratio electrode. Cyclic voltammetry was carried out at varying scan rates of 5 mV/s to 100 mV/s in corresponding potential windows. The GCD analysis was done at different current density values in the same potential windows as the CV analysis.

The **equation (1)** was used to calculate the specific capacitance value from CV [120, 121].

[122].

$$C_s = \frac{\int_{V_1}^{V_2} I(V) dV}{m \cdot v \cdot (V_2 - V_1)} \quad (1)$$

Here I is the current (A), v is the scan rate, ΔV is the potential difference, and m indicates the mass of the active material.

To find the specific capacitance (C_{sp}) from the GCD, normalize the capacitance by the mass of the active material. The equation for the calculation of the specific capacitance C_{sp} (F/g) from GCD in **equation (3)** [123].

$$C_{sp} = \frac{C}{m} = \frac{I \Delta t}{m \Delta V} \quad (3)$$

where m indicates the mass again. Whereas the energy density E_d (W/kg) and power density P_d (Wh/ kg) for supercapacitors can be calculated by these relations **equation (4,5)** [124].

$$E_d = \frac{1}{2} C_{sp} \Delta V^2 \quad (4)$$

$$P_d = \frac{E_d}{\Delta t} \quad (5)$$

3.7. Two electrode Device Fabrication:

To assemble the two-electrode supercapacitor device, an asymmetric configuration was used to test the electrochemical performance of the synthesized materials. The positive electrode utilized the synthesized perovskite oxide-based materials, and activated carbon was used as a counter electrode (both coated on Cu foil). A porous separator (glass fiber) was used as a separator between the two electrodes to avoid short-circuiting while facilitating ionic transport within the electrolyte. 1-Methyl-1-propylpiperidinium bis(trifluoromethane sulfonylimide) was used as an electrolyte because of its wide electrochemical potential window and high ionic conductivity. The electrodes, separator, and electrolyte were inserted into a stainless-steel coin cell to achieve uniform compression and solid contact for minimum resistance. To avoid electrolyte evaporation and keep stability for electrochemical testing, the cell was then sealed.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Tuning Electrochemical Behavior of the LaNiO_3 electrode via Mn-Ru co-doping for Enhanced Energy Storage Performance

4.1.1. X-ray diffraction XRD.

The crystal structure of Manganese and Ruthenium co-doped Lanthanum Nickelate $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ having the ratio of $(x = 0, y = 0)$, $(x = 0.08, y = 0.02)$, $(x = 0.05, y = 0.05)$ and $(x = 0.02, y = 0.08)$ were examined by XRD. Cu- $\text{K}\alpha$ source of x-rays was used, having the wavelength of 1.5406Å for XRD analysis. All the peaks are in good agreement with JCPD: 96-100-0311). The analysis indicates the hexagonal structure of Lanthanum Nickelate and all co-doped samples [125]. The Miller indices of each diffracted plane were assigned as (1 0 -2), (1 1 0), (2 0 2), (2 0 -4), (2 1 4), and (2 0 8) corresponds to the Braggs angle 23.4°, 32.9°, 40.9°, 47.3°, 58.6°, and 69° shown in **Figure 7 a**. No additional peak was observed in the XRD scans of Mn-Ru co-doped LaNiO_3 , which indicates the successful doping of dopant elements (Mn & Ru) in the host crystal.

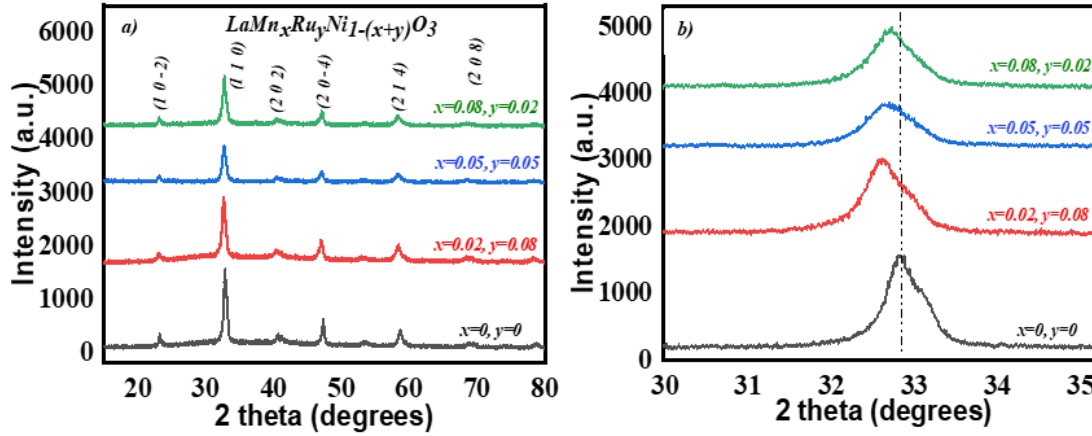


Figure 7 a). XRD patterns of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ b). describes the zoomed view of the most intense diffraction peak of Mn-Ru co-doped Lanthanum Nickelate $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$.

From **Figure 7 b.**, It can be observed that the intense peak (110) of the co-doped Mn-Ru compound shifted towards the left, and it is observed that the ratio $x=0.02$ & $y=0.08$ has the most shifted peak. This is due to the higher radii of Ruthenium, which creates stress in the crystal [126]. To analyze the material's structural properties from XRD, crystalline size, lattice parameters, and unit cell volume have been calculated. The Debye-Scherrer formula is used to find the crystalline size using equation (6) [127].

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (6)$$

where λ is 1.5406 Å, k is the shape factor, which is typically 0.9 for spherical shape, β represents full-width half maximum (FWHM) of peaks and θ is the Bragg's diffraction angle. The crystallite size decreased by increasing the Ru concentration, as shown in Table 1, due to the large FWHM value (broadening of peak). In turn, the crystallinity of the material decreases indicating the material will have an increase in surface area with improved ionic conductivity [128]. To find the lattice parameters, firstly, we will calculate interplanar spacing d_{hkl} Bragg's law equation (7).

$$2d_{hkl}\sin\theta = n\lambda \quad (7)$$

where n represents the order of reflection. To find the lattice parameters of the Hexagonal crystal structure, we will use the relation using equation (8).

$$\frac{1}{d_{hkl}} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (8)$$

where a and c are the lattice parameters and (hkl) are the Miller indices. The results show that the crystallite size decreases with an increase in Ruthenium (Ru) concentration, and the unit cell volume increases. This is due to the higher atomic radii of Ru with respect to Manganese (Mn), resulting in peaks shifting to lower angles [129]. Moreover, the lattice parameters a and c increase with increasing Ru content. Such expansion is due to the larger atomic radii of Ru compared to Mn, which leads to an overall enlargement in the lattice structure.

The strains induced (ϵ) in the crystal lattice due to the incorporation of doping elements can be calculated from the Stokes–Wilson formula equation (9) (**Table 1**) [130].

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad (9)$$

The dislocation density (δ) has been calculated by using equation (10) [131] with the help of crystallite size (D).

$$\delta = \frac{1}{D^2} \quad (10)$$

Table 1. XRD parameters of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (x=0.00, y=0.00), (x=0.02, y=0.08), (x=0.05, y=0.05), (x=0.08, y=0.02)

$\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (x,y)	2θ (degree)	Lattice Parameters (a,c)	Crystallite Size (D) (nm)	Volume ($\text{\AA}^3$)	Lattice Strain (ϵ)	Dislocation density (δ) 1/nm²
(0, 0)	32.8677	(5.446, 13.219)	12.57	339.48	0.558469	0.006326
(0.08, 0.02)	32.7252	(5.469, 13.315)	11.66	344.84	0.604879	0.007361
(0.05, 0.05)	32.6959	(5.473, 13.332)	11.05	345.89	0.638766	0.008194
(0.02, 0.08)	32.6424	(5.482, 13.348)	10.31	347.41	0.685203	0.009399

4.1.2. Scanning Electron Microscopy (SEM)

SEM was carried out to examine the synthesized electrode materials' size and shape surface morphology ($\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$). SEM images of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (**Figure 8(a-h)**) depict the low and high magnification of various doping ratios of Mn and Ru; as seen in the images, all the samples have nano-dimensional morphology with a regular porous structure, albeit with varying particle and pore diameters. In addition, some samples have agglomeration, owing to the high surface energy of Mn as compared to Ru [56, 132]. The samples having Mn to Ru ratio ($x = 0.02$ and $y = 0.08$) in $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ have insignificant agglomeration with a more porous surface as compared to the other samples with larger surface area and are expected to provide a greater surface area for the easy access of electrolyte to the active site for the supercapacitor application. Further, the chemical purity and elemental analysis of the material were examined by mapping and EDX at a scale bar of 25 μm . The results revealed the presence of La, Mn, Ru, Ni, and O elements in all the synthesized samples ($\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$), respectively, with greater homogeneity distribution in the texture without any impurity.

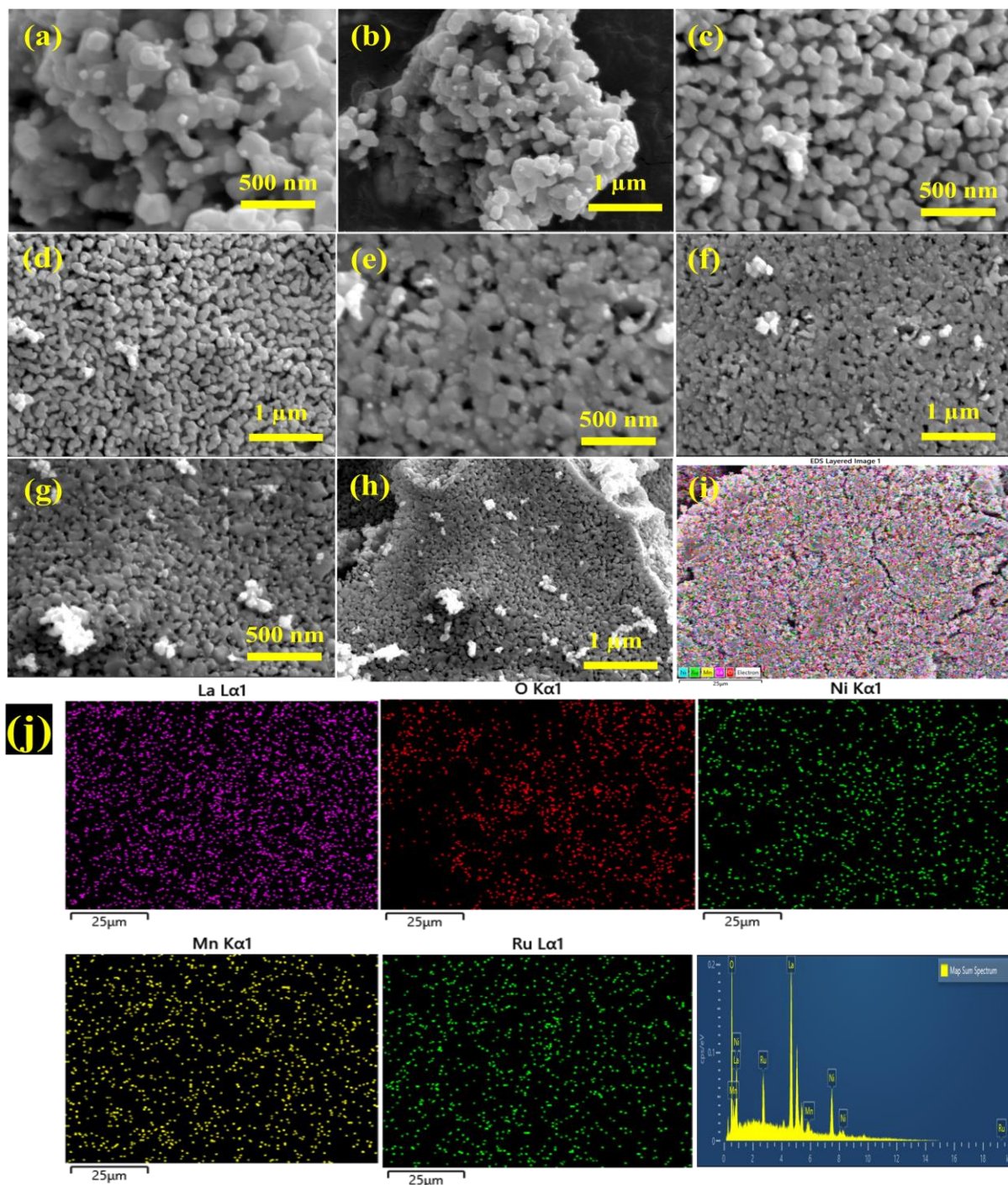


Figure 8. FESEM micrographs of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$, $(x,y)=(0,0)$ (a,b), $(0.02, 0.08)$ (c,d), $(0.05, 0.05)$ (e,f), $(0.08, 0.02)$ (g,h), EDX, and mapping detected a homogenous distribution of Lanthanum (La), Oxygen (O), Nickle (Ni), Manganese (Mn), and Ruthenium (Ru) (j)

4.1.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra recorded over the 600–4000 cm^{-1} range were investigated to confirm the samples' phase composition (**Figure 9**). A pronounced absorption band is observed at 600 cm^{-1} for both pure LaNiO_3 and Mn, Ru co-doped LaNiO_3 samples, which is attributed to the stretching vibrations of Ni-O-Ni bonds in the NiO_6 octahedron of the perovskite-type ABO_3 [133, 134]. All samples show high symmetry with no impurity phases, which is consistent with XRD results. Band at 2350 cm^{-1} corresponds to symmetric stretching of carboxyl C=O bond due to the carbon dioxide adsorbed from the atmosphere [135]. Peaks at 2000–2100 cm^{-1} and 3000 cm^{-1} are not a feature of LaNiO_3 systems. These may indicate impurity phases of C=C (alkyne groups) and OH (hydroxyl group) [136].

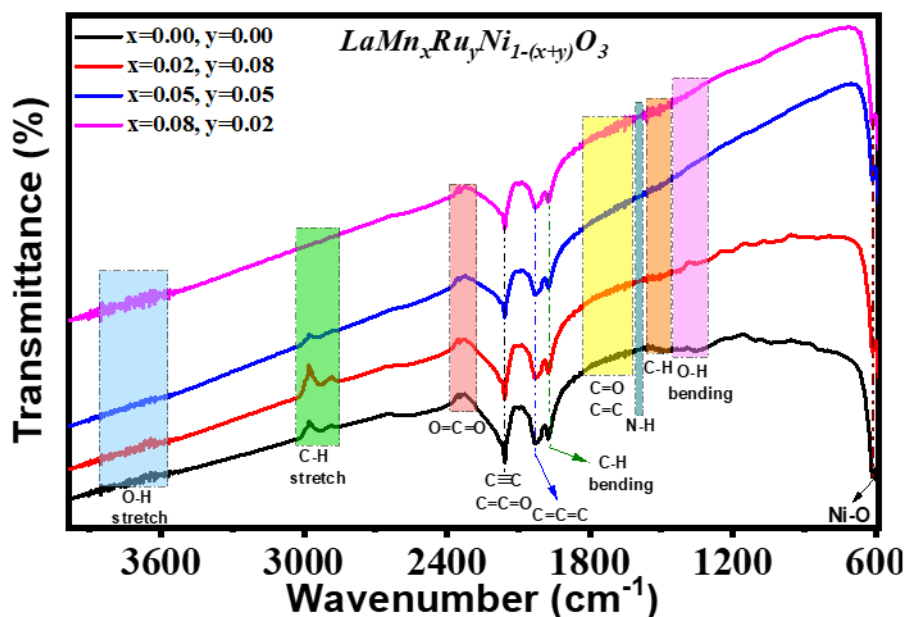


Figure 9. FTIR spectra of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.00, y=0.00$), ($x=0.02, y=0.08$), ($x=0.05, y=0.05$), ($x=0.08, y=0.02$)

4.1.4. X-ray photoelectron spectroscopy (XPS)

XPS analysis of the sample yielding the best electrochemical performance, i.e., $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$, with $(x, y) \sim (0.02, 0.08)$, was investigated to confirm the elemental compositions and electronic structures/oxidation states of the elements. Full scan XPS spectra of the sample are shown in **Figure 10 a.**, whereas high-resolution spectra of O 1s, La 3d, 4d, Mn 2p, Ni 2p, Ni 3p, Ru 3p, and 3d are presented in **Figures 10 b–i**, respectively. The survey scan (**Figure 10 (a)**) exhibits all the constituent elements i.e., La, Ni, Mn, Ru, and O. Binding energy is calibrated with reference to adventitious carbon C 1s peak at 284.5 eV. **Figure 10 (b)** shows deconvoluted core level spectra of O 1s, divided into two peaks at 528.5 eV and 531.5 eV binding energies, indicating different oxygen environments. The high-resolution spectrum of La shows peaks at 854.6 and 851.3 eV, which are identified as La $3d_{3/2}$, while the doublet at 837.8 and 833.7 eV correspond to La $3d_{5/2}$, indicating the oxidation state of +3 [137]. Ni 2p core level spectra show a 3+ valance state with a $2p_{1/2}$ peak at 869 eV and a $2p_{3/2}$ peak at 853.5 eV, accompanied by satellite lines at 878.5 eV and 862.5 eV, respectively. $2p_{1/2}$ (636.5 eV) and $2p_{3/2}$ ((641.5 eV)) spectral lines of Mn also show an oxidation state of +3 for B-site doping [138]. The presence of a single peak of $3p_{1/2}$ at 460.6 eV in the Ru- $3p_{3/2}$ region (**Figure 10 (h)**) exhibits the valence state of +3 for doped Ru ions like that in LaRuO_3 system [139]. The peak at 285 eV represents the presence of Ru $3d_{3/2}$. Low energy peaks represent oxygen ions bound to Ni ions, whereas higher energy peaks may have resulted from oxygen vacancies created to maintain charge neutrality.

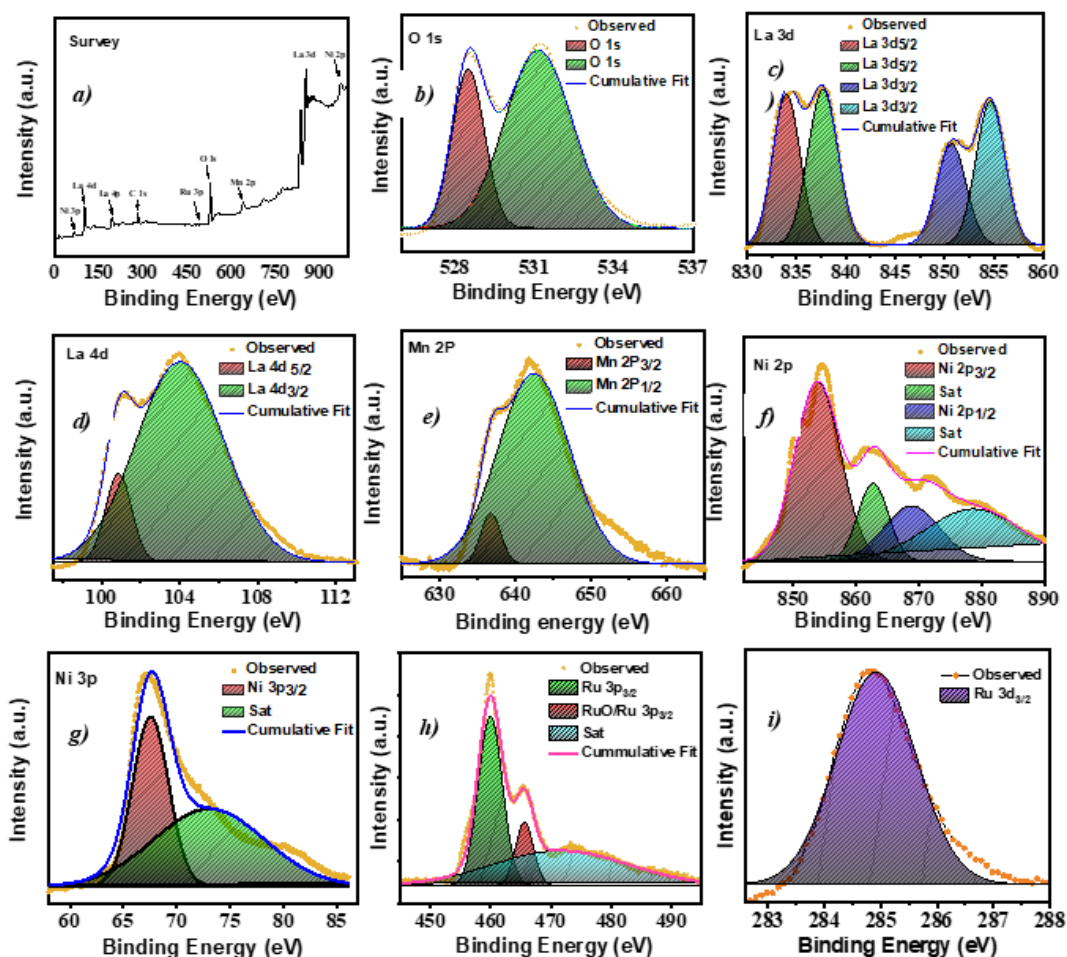


Figure 10. XPS spectra of $\text{LaMn}_{0.02}\text{Ru}_{0.08}\text{Ni}_{0.9}\text{O}_3$ ($x=0.02$, $y=0.08$), a) survey spectra, b) O 1s, c) La 3d, d) La 4d, e) Mn 2p, f) Ni 2p, g) Ni 3p, h) Ru 3p, i) Ru 3d respectively.

4.1.5. Three electrode cell configurations

a) Cyclic Voltammetry (CV)

The electrochemical performance of prepared $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ electrodes coated on Ni-foam was first measured in a three-electrode system. The measurements were conducted in 1M KOH aqueous electrolyte. The cyclic voltammetry (CV) measurement is employed to study the charge storage capability and chemistry. The CV curves of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ electrodes were obtained in a fixed potential window of 0-0.55 V in various scan rates of 5, 10, 20, and 50 mV/s, as shown in **Figure 11 (a-d)**. Semi-rectangular shapes in all prepared electrodes strongly indicate the

presence of a pseudocapacitive nature. In all the CV loops, Prominent peaks are due to the faradic reactions. They are because of the change in oxidation states of the present transition oxides sitting at the B-site, which describes the reduction and oxidation response between electrode-electrolyte interfaces. This change in oxidation states of B-site cations is responsible for the movement of oxygen vacancies throughout the structure, and these sites behave as charge carriers. The increase in oxygen vacancy movement in perovskite oxide pseudocapacitor can lead to an increase in C_{sp} and, hence, an enhancement in overall electrochemical performance. Furthermore, the redox characteristic is an indication of the conductivity of mixed ions and electrons. The doping/co-doping on the B-site cation can change the oxidation state due to differences in ionic and valence radius; hence, this will change the specific capacitance. Detailed analysis of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ CV data revealed that $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) has the highest area under the CV curve in comparison to other produced materials and hence has highest specific capacitance.

It can be observed that when the scan rate was increased, the shape of the curves was almost unchanged, representing that all the electrodes had good kinetic reversibility. Even at high scan rates, the redox peaks are visible, demonstrating the excellent reaction kinetics for energy storage. Furthermore, from the CV curves (**Figure 11 (a-d)**) faradic peaks become higher with the increase in scan speed, and the difference between anodic and cathodic peak potential also increases with the scan rates. A small difference in peak potentials is an indication of faster electron transfer kinetics and is a characteristic of a reversible process. The large difference in peak potential indicates slow electron transfer kinetics and is a characteristic of a quasi-reversible or irreversible process. It may involve some complex mechanisms, multiple steps, or slow chemical reactions following the electron transfer. The peak potential differences for $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.00$, $y=0.00$), ($x=0.02$, $y=0.08$), ($x=0.05$, $y=0.05$), ($x=0.08$, $y=0.02$) are 0.145, 0.110, 0.120, and 0.125

respectively at a scan rate of 5mV/s. These values indicate that (x=0.02, y=0.08) has faster electron transfer kinetics than other prepared electrodes.

Moreover, specific capacitance values calculated from the CV curves are 704, 990, 945, and 925 F/g for $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (x=0.00, y=0.00), (x=0.02, y=0.08), (x=0.05, y=0.05), (x=0.08, y=0.02) respectively. The (x=0.02, y=0.08) provided a more Prominent faradic peak which built strong interaction between the electrode-electrolyte interface. Also, (x=0.02, y=0.08), has a larger crystal structure (larger lattice parameters) with a more porous surface. So it can accommodate more electrolyte ions. These factors are responsible for the highest specific capacitance in (x=0.02, y=0.08). We observed that C_{sp} decreases with the increase in scan rates. This is because, at a low scan rate, electrolyte ions have enough time to complete redox reactions and diffuse in the electrode materials. On the other side, at a high scan rate, specific capacitance has a low value because of the unavailability of active sites and limited time for the ions to adsorb and desorb on the surface to complete the redox reaction. Based on the above analysis, the enhanced electrochemical performance of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (x=0.02, y=0.08) is due to higher ions adsorption-desorption on the electrode surface, and intercalation/deintercalation of hydroxyl (OH^-) ions on the surface. The morphology of (x=0.02, y=0.08) also provides more active sites for the charge storage process. These processes make it easier for ions and electrons to move quickly during the electrochemical process in (x=0.02, y=0.08).

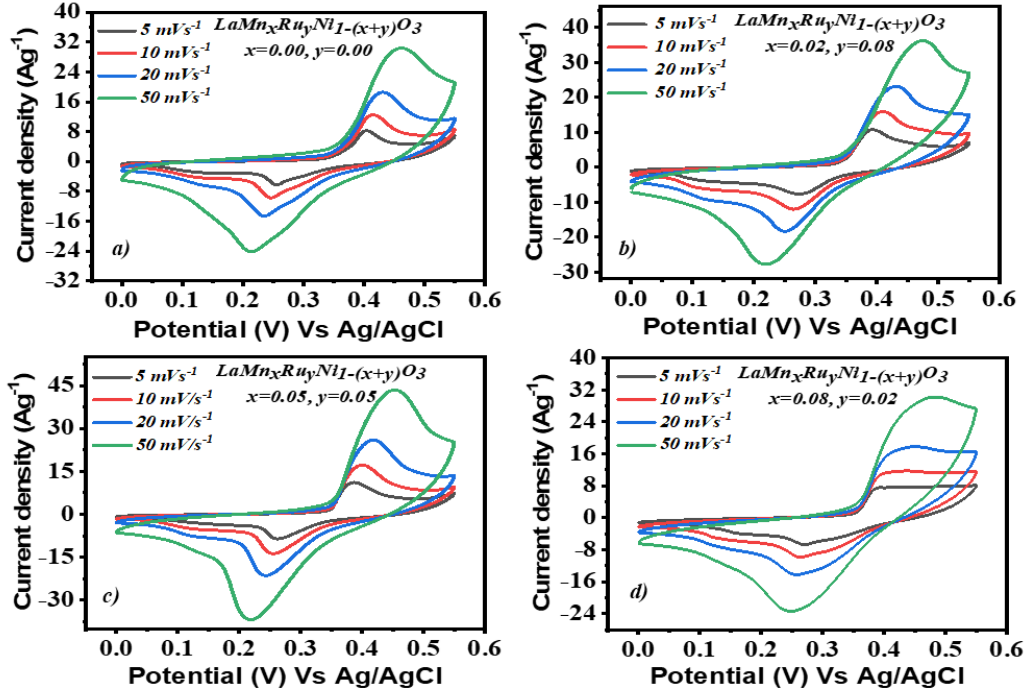


Figure 11. CV curves of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$ a) $(x,y)=(0,0)$, $(0.02, 0.08)$, $(0.05, 0.05)$, $(0.08, 0.02)$ (a-d).

The specific capacitance is due to diffusion-controlled behavior and capacitive-controlled behavior. Diffusion-controlled behavior occurs when the reaction is limited by the diffusion of ions from the electrolyte to the electrode surface. While capacitive controlled behavior occurs when the charge is stored by electrostatic adsorption of ions at the electrode-electrolyte interface. Dunn's equation can compute the percentage diffusion and capacitive controlled behavior equation (11).

$$I = k_1V + k_2V^{1/2} \quad (11)$$

Where k_1 and k_2 are slope and intercept of $V^{1/2}$ vs $1/V^{1/2}$. k_1V term related to capacitive while $k_2V^{1/2}$ term related to the diffusion-controlled behavior. **Table 2.** shows the capacitive and diffusion-controlled capacitance at different scan rates. The capacitive behavior of electrode materials is shown with orange, blue color, while diffusion-controlled behavior is shown with

green blue color in **Figure 12 (a-d)**. We can see that at a low scan rate, diffusion behavior is more; this is because at a low scan rate, intercalation and deintercalation of electrolyte ions are more common. The distinct percentage contribution is also shown in **Figure 12 (a-d)**.

Table 2. Percentage Capacitive and diffusion contribution of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$ (x,y)=(0,0), (0.02, 0.08), (0.05, 0.05), (0.08, 0.02)

Scan rate	(x=0.00, y=0.00)		(x=0.02, y=0.08)		(x=0.05, y=0.05)		(x=0.08, y=0.02)	
	%Capacitive	%Diffusion	%Capacitive	%Diffusion	%Capacitive	%Diffusion	%Capacitive	%Diffusion
5	15	85	15	85	7	93	10	90
10	34	66	21	79	10	90	14	86
20	42	58	27	73	14	86	18	82
50	53	47	37	63	20	80	26	74

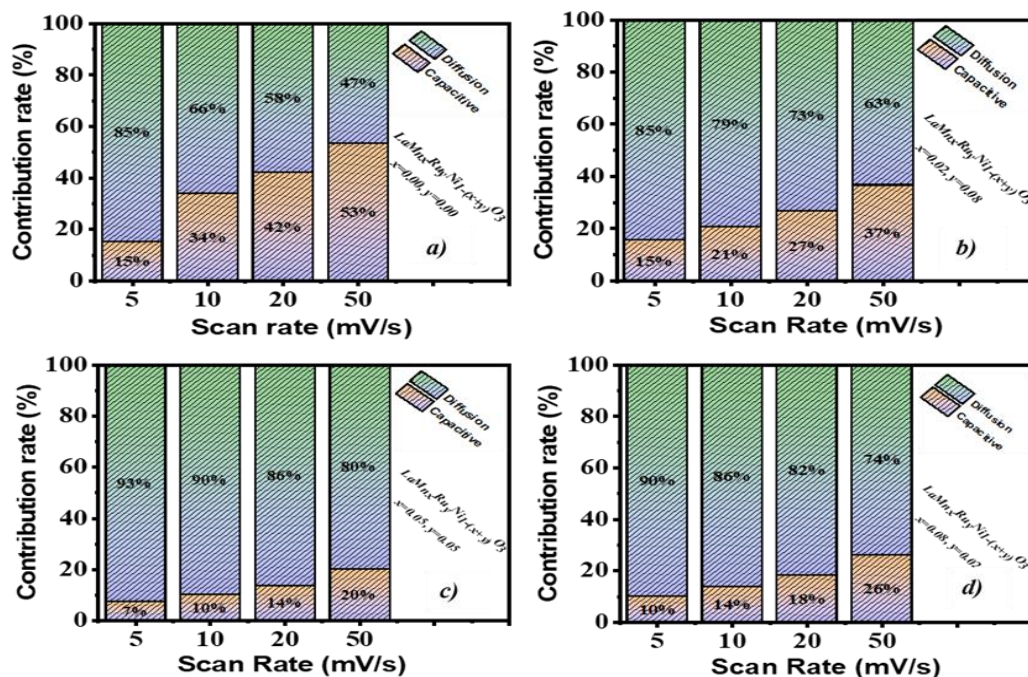


Figure 12. Capacitive and Diffusion contribution of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$, (x,y)= (0,0), (0.02, 0.08), (0.05, 0.05), (0.08, 0.02) (a-d) respectively.

b) Galvanostatic Charge-Discharge (GCD):

To further examine the electrochemical performance of prepared perovskite oxides, The GCD analysis was employed under the same conditions as CV In a 3-electrode setup with 1M KOH as an electrolyte. A detailed GCD analysis of synthesized materials is appeared in **Figure 13 (a-e)**. The non-linear triangular shape indicates the pseudocapacitive behavior in all materials. This behavior agrees with the behavior observed in CV curves. It can also be observed that charge curves do not mirror the discharge curves' symmetry. This is due to the surface redox reactions taking place on the electrode surface [140]. $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) showed higher discharge time (Figure 8 b.) as compared to other prepared compositions (at the same current density) due to which, it showed the highest electrochemical performance (Specific capacitance, energy & power density). The specific capacitance calculated from GCD curves are 349.10, 632.72, 545.53, and 501.18 F/g for $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.00$, $y=0.00$), ($x=0.02$, $y=0.08$), ($x=0.05$, $y=0.05$), ($x=0.08$, $y=0.02$) respectively at the current density of 4 A/g shown in **Table 3**. Excellent electrochemical performance in $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) is explained due to more redox reactions than pure LaNiO_3 and more oxygen vacancies are present in the crystal structure. Also, this composition has the highest electrochemical performance because of the larger lattice parameters, as observed from the peak shift toward the lower angle in the XRD graph. Also, the less agglomerated structure of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) provides better ionic transport compared to other compositions. It was observed that $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) has the highest C_{sp} at all current densities (**Figure 13 f**). These results are aligned with the CV results. It was observed that the IR drop in $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) is lesser than in other compositions, and the IR drop decreases from

high current density to low current density. This is because of the availability of more time during the ion exchange mechanism at lower current densities. From the slope of GCD curves, the Discharge curve (**Figure 13 (a-e)**) has a plateau region between the potential ranging from 0.42 to 0.52 V, representing the redox reactions at the electrolyte-electrode interface [61, 141].

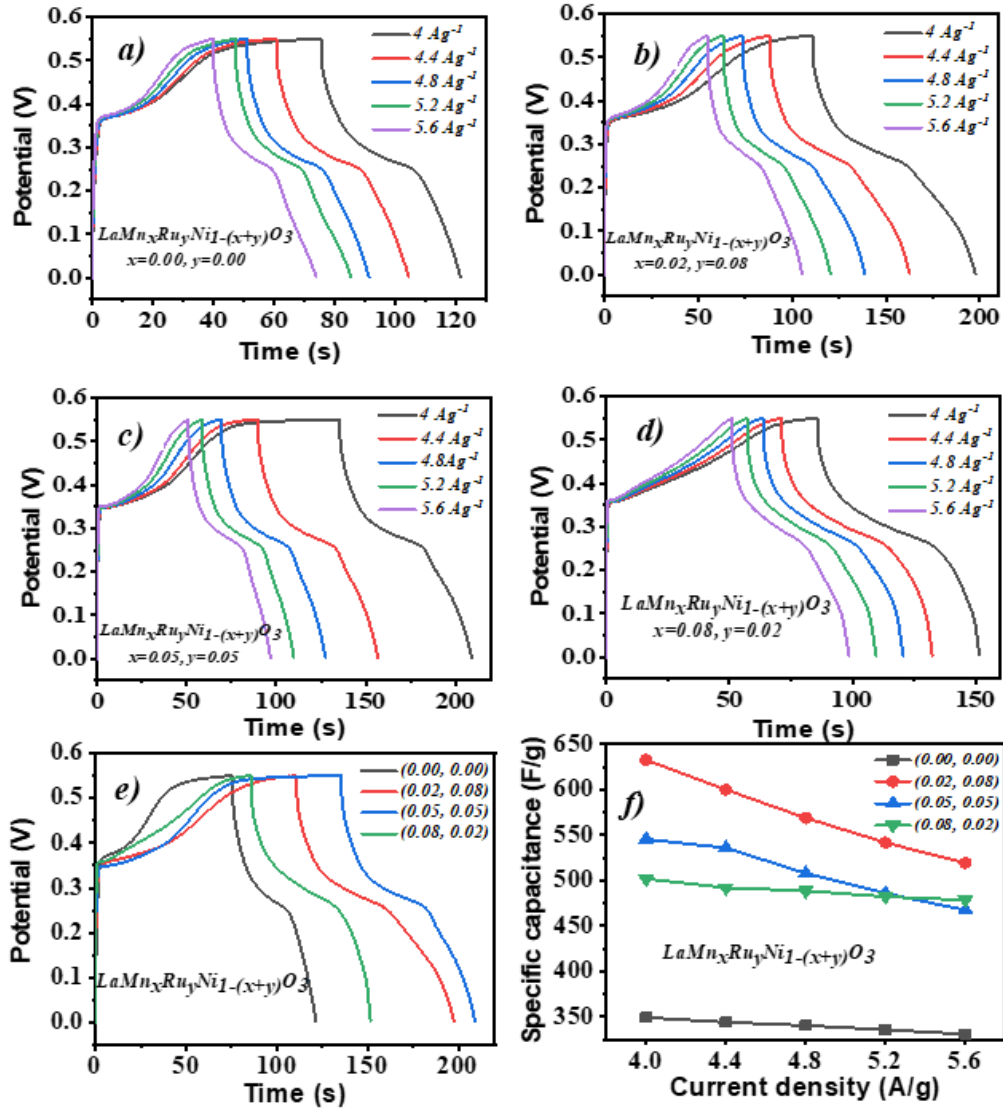


Figure 13. Galvanostatic charge-discharge (GCD) profiles of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$ (x,y) = (0,0), (0.02, 0.08), (0.05, 0.05), (0.08, 0.02) (a-d) respectively at various current densities, GCD at 4 A/g (e), Specific capacitance vs current density (f)

The GCD curves are helpful in finding many parameters like C_{sp} , energy, and power density from cathodic-anodic curves. **Figure 13 f.** shows the specific capacitance of all compositions at various current densities and it demonstrates the decrease in specific capacitance with current density, this is because the chemical interaction of perovskite oxides is only limited to its exterior surface at

high current densities. As a result, fewer active sites are available for the electrolyte ions, and specific capacitance decreases.

Table 3. Electrochemical parameters of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (x,y)= (0,0), (0.02, 0.08), (0.05, 0.05), (0.08, 0.02)

Material $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$	Current density (A/g)	Specific capacitance (F/g) at 4 A/g	Power density (W/kg)	Energy density (Wh/kg)
x=0.00, y=0.00	4	349.10	1132.40	14.66
x=0.02, y=0.08	4	632.72	1139.28	26.58
x=0.05, y=0.05	4	545.53	1100.46	22.91
x=0.08, y=0.02	4	501.18	1100.01	21.08

c). Electrochemical Impedance Spectroscopy (EIS):

The electrochemical impedance analysis was employed to study the electrochemical behavior of as-synthesized perovskite oxide compounds with the help of a Nyquist plot as shown in **Figure 14 a**. The EIS measurement was performed between 0.1 Hz-100 MHz. EIS is used to understand the reaction kinetics and ion transport behavior of electrode materials using the plot between Z' (real) and Z'' (imaginary) impedance components to check the frequency response of the electrodes [142]. The Nyquist plot can be split into two regions i.e., high-frequency and low-frequency regions. The intercept at the X-axis represents the ionic resistance (R_s) that electrolytes offer at the electrode-electrolyte surface during the movement of ions. The diameter of the semi-circle at the high-frequency region gives the charge transfer resistance (R_{ct}) [143, 144], while the slope in the Nyquist plot represents the diffusive impedance. The wide diameter semicircle represents the resistance dominance, whereas its small diameter represents the capacitive dominance. Additionally, the Nyquist plot shows steeply rising behavior at low-frequency regions, while a semicircle is detected at high-frequency regions. Such characteristics indicate a capacitive

nature [145]. The table below shows that compared to other compositions, $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) has the lowest Charge transfer resistance value (R_{ct}). At low-frequency region, the Nyquist plot should be parallel to the Z'' axis for an ideal case [146]. The shape is nearly parallel for $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$), indicating the capacitive nature and further confirming the domination of the capacitive nature. **Figure 14 b.** shows the Ragon plot of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ (x,y)= (0,0), (0.02, 0.08), (0.05, 0.05), (0.08, 0.02).

Table 4. EIS parameters of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$

Material $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$	Series resistance (R_s) (Ω)	Charge transfer resistance (R_{ct}) (Ω)
$x=0.00$, $y=0.00$	0.93	1.92
$x=0.02$, $y=0.08$	0.82	1.60
$x=0.05$, $y=0.05$	0.72	1.66
$x=0.08$, $y=0.02$	0.85	1.8

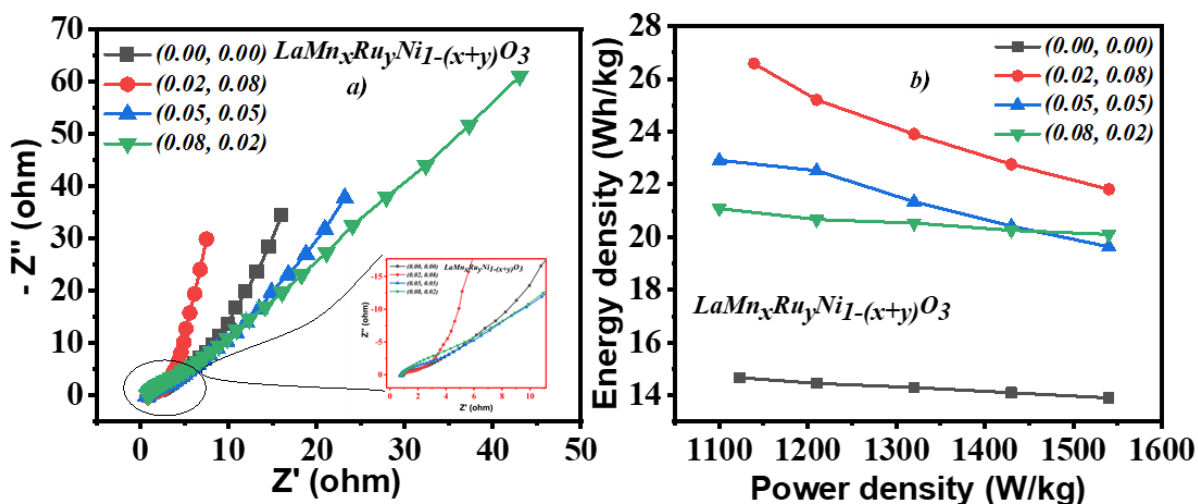


Figure 14. Nyquist plots (a), Ragone plot (b) for $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$ (x,y)= (0,0), (0.02, 0.08), (0.05, 0.05), (0.08, 0.02).

4.1.6. Two Electrode configuration

A two-electrode device was fabricated to estimate the practical performance of as-synthesized co-doped perovskite material in an asymmetric supercapacitor configuration. The device featured a

perovskite material as the anode and activated carbon as the cathode. This design was selected to optimize both the energy and power density, with activated carbon having a high surface area and conductivity that can complement the pseudocapacitive properties of perovskite. The two materials were coated onto copper foil substrates to provide good conductivity and compatibility with the electrolyte. **Figure 15 a.** shows the cyclic voltammetry (CV) curves and redox peaks, demonstrating that pseudocapacitor behavior is mainly responsible for charge storage. The potential window was enhanced to 0-2.7 V, by employing the electrolyte of 1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (MPB) for acquiring fast ion mobility and a steady electrochemical environment. The charge-discharge curve in **Figure 15 b.** shows the high stability and low IR drop of the fabricated device. In **Figure 15 c.** the Electrochemical Impedance Spectroscopy (EIS) data confirms the capacitance-like nature with a slanted profile as shown in **Figure 15 c.** A Nyquist plot result presents a vertical line in the low-frequency region, further confirming excellent capacitive behavior and limited resistive losses (ideal traits for high-performance supercapacitors).

The optimized device was also tested at various current densities, shown in **Figure 15 b.** At 1 A/g current density, the specific capacitance was found to be 81.48 F g^{-1} , demonstrating that the Mn-Ru co-doped perovskite-based supercapacitor device has outstanding charge-storage performance in practical cell configurations. Additionally, it had an E_d of 82.5 Wh/kg, a key metric for real-world applications, and a P_d of 1350 W/kg. From the Nyquist plot (**Figure 15 c.**), the Charge transfer resistance is 9.2 ohms, and the series resistance is 16 ohms, **Figure 15 d.** shows Ragone plot comparing our device performance with the reported supercapacitor devices. The exceptional electrochemical performance of $\text{LaMn}_x\text{Ru}_y\text{Ni}_{1-(x+y)}\text{O}_3$ ($x=0.02$, $y=0.08$) is compared with the

previous literature findings shown in **Table 5**. These values indicate a high potential of the Mn-Ru co-doped LaNiO_3 perovskite for next-generation energy storage devices.

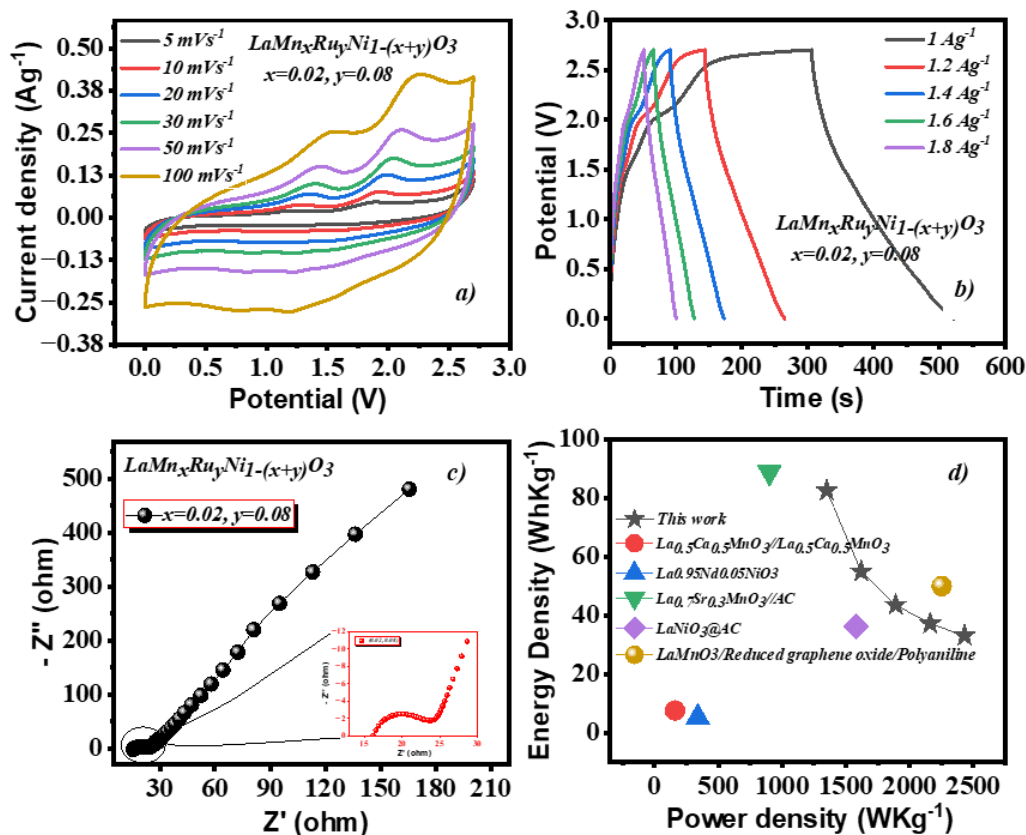


Figure 15. Cyclic voltammetry (a), Galvanostatic charge-discharge at various current densities (b), Electrochemical impedance spectroscopy (c), and Ragone plot (d) for $\text{LaMn}_{0.02}\text{Ru}_{0.08}\text{Ni}_{0.9}\text{O}_3//\text{AC}$ based device.

Electrode material	Electrolyte	Capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Reference
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3//\text{AC}$	1 M Na_2SO_4	197	88.7	900	[147]
$\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3//\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$	1 M KOH	18	3.6	120	[148]
$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3//\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$	1 M KOH	21.7	7.6	160	[140]
$\text{La}_2\text{CuCoO}_6$	2 M KOH	259.4	-	-	[149]

$\text{La}_{0.95}\text{Nd}_{0.05}\text{NiO}_3$	-	32.24	5.32	339.45	[55]
$\text{LaMn}_{0.02}\text{Ru}_{0.08}\text{Ni}_{0.9}\text{O}_3//\text{AC}$	MPB	81.48	82.5	1350	Present work

Table 5. Comparison of $\text{LaMn}_x\text{Ru}_y\text{NiO}_3$ (x,y)= (0.02, 0.08), with the literature

4.2. Electrochemical Performance of La_2MnXO_6 (X=Co, Fe) Double Perovskite Supercapacitors:

4.2.1. X-ray Powder Diffraction (XPRD)

The structural study was conducted using the X-ray Diffractometer (XRD) within the $10^\circ - 90^\circ$ range. The instrument utilized Cu – $K\alpha$ radiation with a wavelength of $\lambda = 1.5406 \text{ \AA}$. The X-pert high score software was used to analyze data. The crystal structure of $\text{La}_2\text{MnCoO}_6$ and $\text{La}_2\text{MnCoO}_6$ double perovskite over the 2θ range of $10^\circ - 90^\circ$ is examined using the XRD analysis and is given in **Figure 16**. The prominent diffraction peaks identified at $2\theta = 22.47^\circ, 27.44^\circ, 32.19^\circ, 39.78^\circ, 46.55^\circ, 52.22^\circ, 57.82^\circ, 67.96^\circ, 77.72^\circ$ correspond to (110), (111), (112), (220), (202), (114), (312), (224), (116) planes respectively and agrees to JCPDS no. 01-074-7468. Based on PXRD tests, the analysis of sample $\text{La}_2\text{MnCoO}_6$ reveals the presence of monoclinic $\text{La}_2\text{MnCoO}_6$ (**Figure 16**). The LMCO structure has two distinct intensity peaks corresponding to the (020) and (112) planes. The monoclinic structure of the LMCO double perovskite precisely corresponds to the P21/n space group. The lattice parameters, with values of $a = 5.5253 \text{ \AA}$, $b = 5.4748 \text{ \AA}$, and $c = 7.7671 \text{ \AA}$, as well as the atomic position parameters, are depicted in **Table 6**.

Figure 16 depicts the XRD pattern of $\text{La}_2\text{MnFeO}_6$ that was analyzed using the JCPDS matching with X-pert high score software to ascertain the structural characteristics. The crystallographic data of $\text{La}_2\text{MnFeO}_6$ was refined using the crystallographic data from $\text{La}_2\text{MnFeO}_6$ (JCPDS #01-072-8296) to determine the precise positions of the atoms in the unit cell. The prominent

diffraction peaks identified at $2\theta = 22.39^\circ, 31.98^\circ, 39.52^\circ, 46.09^\circ, 51.96^\circ, 57.4^\circ, 67.4^\circ, 72.13^\circ$, and 76.75° correspond to (101), (200) & (112), (202), (220), (131), (312), (400), (331), and (240) planes respectively. The unit cell of $\text{La}_2\text{MnFeO}_6$ is classified as a double perovskite structure. Based on PXRD tests, the analysis of sample $\text{La}_2\text{MnFeO}_6$ reveals the presence of monoclinic $\text{La}_2\text{MnFeO}_6$ (**Figure 16**). The LMFO double perovskite has a monoclinic structure, specifically belonging to the P21/n space group. The lattice parameters, with values of $a = 5.5491 \text{ \AA}$, $b = 5.5573 \text{ \AA}$, and $c = 7.7835 \text{ \AA}$, as well as the atomic position parameters, are provided in **Table 7**. The W-H plot is depicted in Figure 3 and plotted between $\sin(\theta)$ on the X-axis and $\beta(\cos \theta)$ on the Y-axis. A linear fit was done to find the y-intercept and slope to estimate the particle size and strain of LMCO and LMFO, as shown in **Tables 6 & 7**, respectively.

The Debye-Scherrer formula was employed to determine the average crystallite size (D) of LMCO & LMFO nanorods. The formula is given by equation (14).

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \quad (12)$$

$$n\lambda = 2d \sin \theta \quad (13)$$

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (14)$$

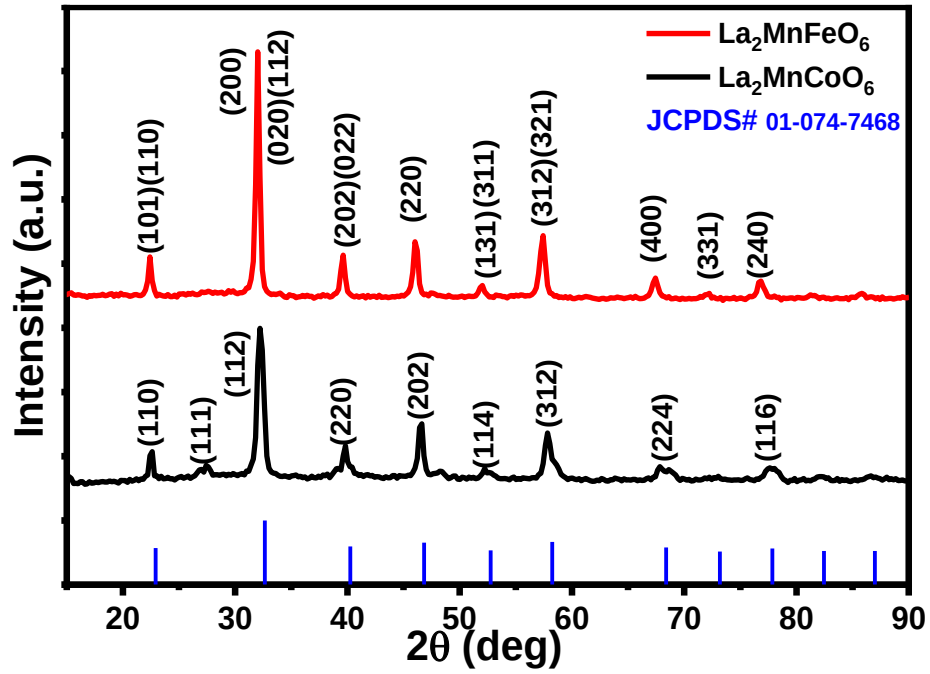


Figure 16. XRD pattern of LMCO and LMFO

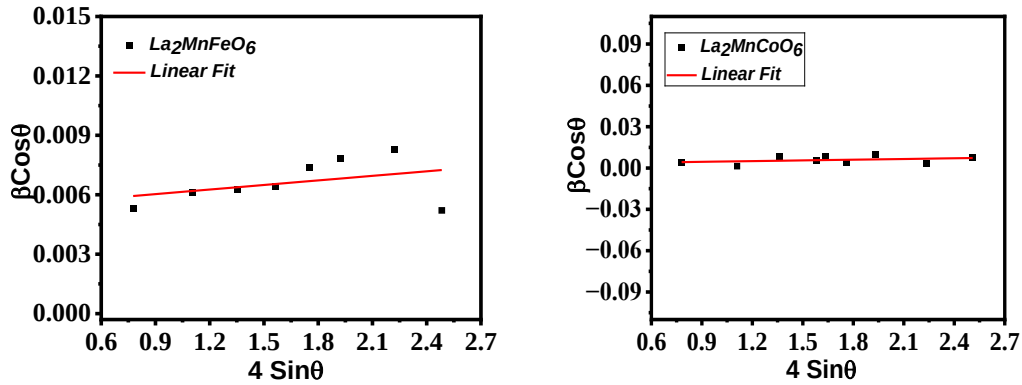


Figure 17. Williamson-Hall analysis of La₂MnFeO₆ and La₂MnCoO₆

Table 6. The lattice and atomic position parameters for La₂MnCoO₆

Peak no	2θ	d = $\lambda/(2*\sin\theta)$	β	D_{av} (nm)	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Density g/cm ³ (ρ)	$\epsilon \times 10^{-4}$ Strain
1	22.475	3.951	0.25		5.517	5.528	7.805	238.03	6.693	17.2
2	32.19	2.777	0.617							
3	39.78	2.263	0.49							
4	46.558	1.948	0.33	179.8		$\beta = 89.926^\circ$				
5	48.31	1.882	0.54							

6	52.22	1.750	0.89			$\alpha=\gamma=90^\circ$			
7	57.82	1.593	0.62						
8	67.96	2.426	0.25						
9	77.72	2.236	0.54						

Table 7. The lattice and atomic position parameters for $\text{La}_2\text{MnFeO}_6$

Peak no	2θ	d =λ/(2*Sinθ)	β	D _{av} (nm)	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Density g/cm ³ (ρ)	ε× 10 ⁻⁴ Strain
1	22.39	3.966	0.31		5.549	5.557	7.783	239.99	6.710	7.6
2	31.983	2.795	0.362							
3	39.521	2.278	0.38							
4	46.09	1.967	0.4	21.575		β= 89.931°				
5	51.96	1.758	0.47							
6	57.4	1.603	0.51			α=γ=90 °				
7	67.4	1.388	0.57							
8	76.75	1.240	0.38							

4.2.2. Field Emission Scanning Electron Microscopy (FESEM)

FE-SEM images of prepared LMCO and LMFO nanorods are depicted in **Figure 18**. **Figure 18** (a, b, & c) shows that LMCO nanorods are irregular and have nanosized lengths of 50-150 nm. Some mesopores and micropores are formed in the LMCO. It can be seen that surfaces are spongy, and pores can be seen in the micrograph. It can be discovered that prepared LMCO powders are mainly formed of aggregated nanorods. **Figures 18** (d, e, & f) depict the FESEM images of LMFO nanorods. It can be observed that prepared LMFO nanorods are mostly regular in shape, with rod lengths ranging from 50-100 nm. LMFO has mostly mesopores. This porosity distribution is more suitable than LMCO. These mesopores enhance contact between the electrolyte and prepared LMFO double perovskite, exposing more active sites and promoting charge transfer. This results in more electrochemical reactions between the electrolyte and electrode surfaces. As a result, we can expect more redox reactions in LMFO than in LMCO.

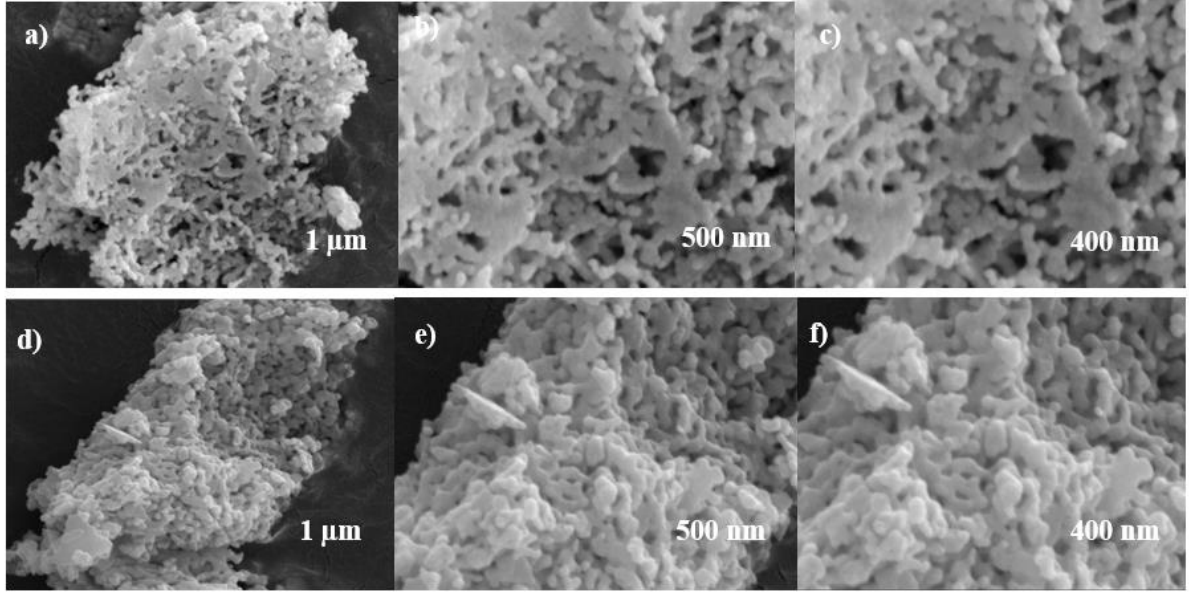


Figure 18. FESEM images of LMCO (a, b, & c) and LMFO (d, e, & f)

4.2.3. Optical Properties- UV-Visible

The DRS-UV-visible spectrum of $\text{La}_2\text{CoMnO}_6$ & $\text{La}_2\text{FeMnO}_6$ was recorded for the optical properties. The optical band gap is determined using Tauc's relation.

$$(\alpha h\nu) = K(h\nu - E_g)^n \quad (15)$$

α represented the absorption coefficient. The dependent parameter is denoted as K , $h\nu$ represents the energy of the incident photon, E_g represents the optical bandgap, and the values of n are as follows: $n = 2, \frac{1}{2}$ & $\frac{3}{2}, \frac{3}{2}$ for direct & indirect allowed transition and direct and indirect forbidden transition, respectively. Where $\alpha h\nu$ represents the measured reflection coefficient and represents the energy of the incident photon.

Perovskites typically exhibit direct allowed transitions, resulting in a value of $n = \frac{1}{2}$. The bandgap, with a value of 1.38 & 1.24 eV for $\text{La}_2\text{CoMnO}_6$ & $\text{La}_2\text{FeMnO}_6$ (**Figure 19**) respectively, is

determined using the Tauc's plot $((\alpha h\nu)^n$ versus $h\nu$). But also calculated the indirect allowed transition for $\text{La}_2\text{CoMnO}_6$ & $\text{La}_2\text{FeMnO}_6$ using $n = 2$ which gives the values of 0.81 & 0.95 eV respectively. This is done by projecting the tangent line on $(\alpha h\nu)^2$ to the X-axis in **Figure 20**. The detected energy band gap in the sample has significant implications for developing photovoltaic devices and light-harvesting technologies.

The value of the direct bandgap is assessed by extrapolating the linear segment of the graph called Tauc's plot by Mott & Dev [150]:

$$(\alpha h\nu)^{\frac{1}{n}} = K(h\nu - E_g) \quad (16)$$

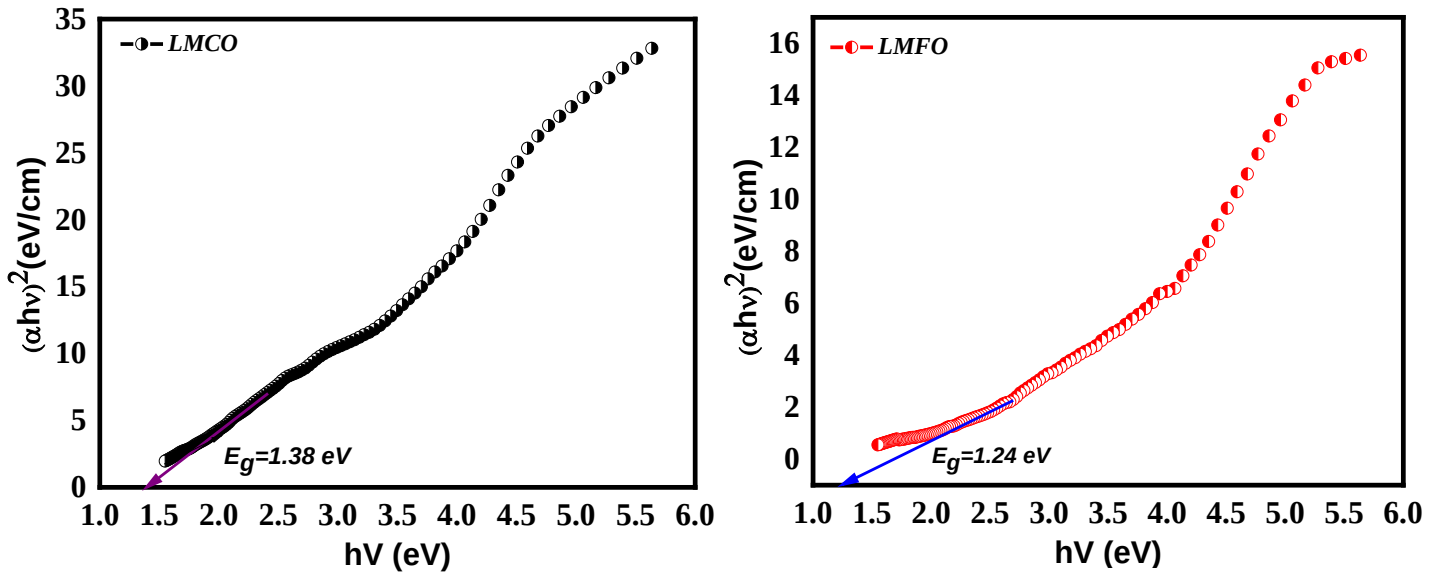
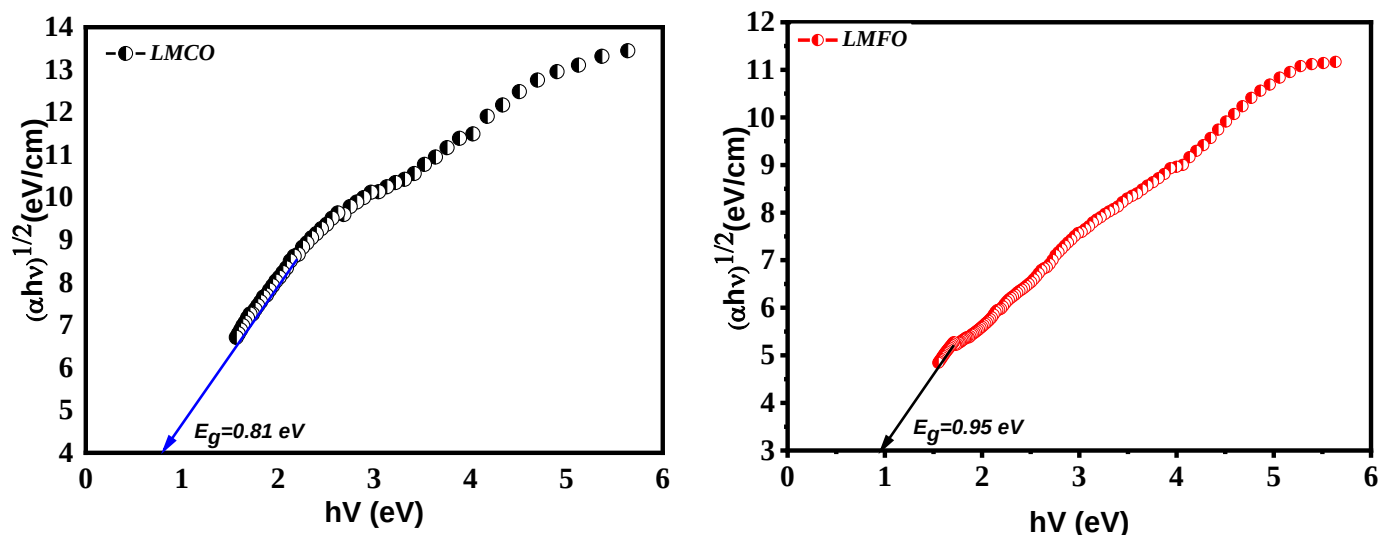


Figure 19. Direct bandgap of a) $\text{La}_2\text{MnCoO}_6$ and b) $\text{La}_2\text{MnFeO}_6$

Figure 20. Indirect bandgap of a) $\text{La}_2\text{MnCoO}_6$ and b) $\text{La}_2\text{MnFeO}_6$

4.2.4. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR analysis can identify unknown materials by comparing the obtained spectrum with a reference library unique for each molecular bond. It can also help identify functional groups present in a compound. **Figure 21** shows FTIR spectra of LMCO and LMFO nanorods. The



LMCO shows a strong absorbance peak around 588 cm^{-1} due to the Mn-O octahedra's asymmetric stretching mode and Co-O's vibrational bending. Meanwhile, LMFO shows a strong absorbance peak of around 560 cm^{-1} , attributed to Fe-O octahedra's vibrational bending. This type of spectra was also reported by Saqlain A. Dar and his team [151]. Small peaks at 1390 cm^{-1} represent O-H stretching and vibration bands.

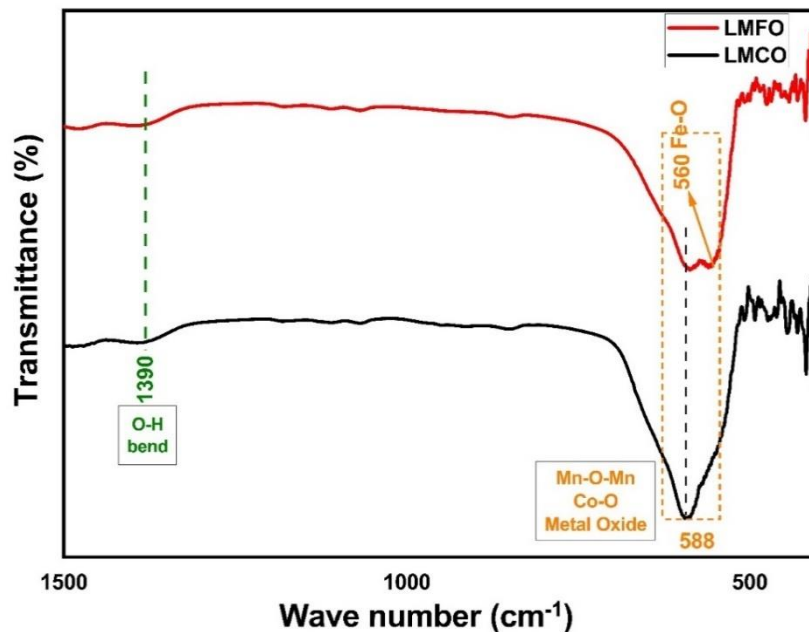


Figure 21. FTIR spectra of La₂MnCoO₆ & La₂MnFeO₆

4.2.5. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was used to understand further the composition and oxidation states of the synthesized best-performance La₂MnFeO₆ double perovskite material, as shown in **Figures 22 (a-e)**. **Fig. 22a** shows the survey spectrum, which tells about the existence of Lanthanum (La), Manganese (Mn), Iron (Fe), and Oxygen (O) elements in the double perovskite material. **Figures 22 (b-e)** show the deconvoluted spectrum of each element in synthesized La₂MnFeO₆ double perovskite. In **Figure 22b**, we noticed two prominent peaks due to spin-orbit coupling at 642.12 eV and 653.71 eV ascribed to Mn 2p_{3/2} and Mn 2p_{1/2}, signifying Mn³⁺ oxidation state, respectively [152, 153]. **Figure 22c** shows the deconvoluted spectrum of Fe at a

lower binding energy of 710.95 eV and higher binding energy of 724.38 eV due to spin-orbit coupling, attributed to Fe 2p_{3/2} and Fe 2p_{1/2} with an oxidation state of Fe³⁺ [153]. The deconvoluted peaks of Fe also have a satellite peak at a binding energy of 718.27 eV. In **Figure 22d**, we observed two notable peaks with multiple splitting at binding energies of 834.67 eV/ 838.41 and 851.45 eV/ 855.19 eV, respectively, corresponding to La 3d_{5/2} and La 3d_{3/2} showing La³⁺ oxidation state [153, 154]. Further, the O 1s spectrum deconvoluted into two distinct peaks in **Figure 22e** confirms the O²⁻ oxidation states with binding energies of 529.39 eV and 531.37 eV corresponding to metal-oxygen bond and absorbed OH oxygen species, respectively [153]. Furthermore, we detected two peaks with a lower binding energy of 779.67 eV and a higher binding energy of 795.34 eV when we fitted the Co 2p peak of the LMCO double perovskite, indicating a Co³⁺ oxidation state (**Figure 22f**) [155].

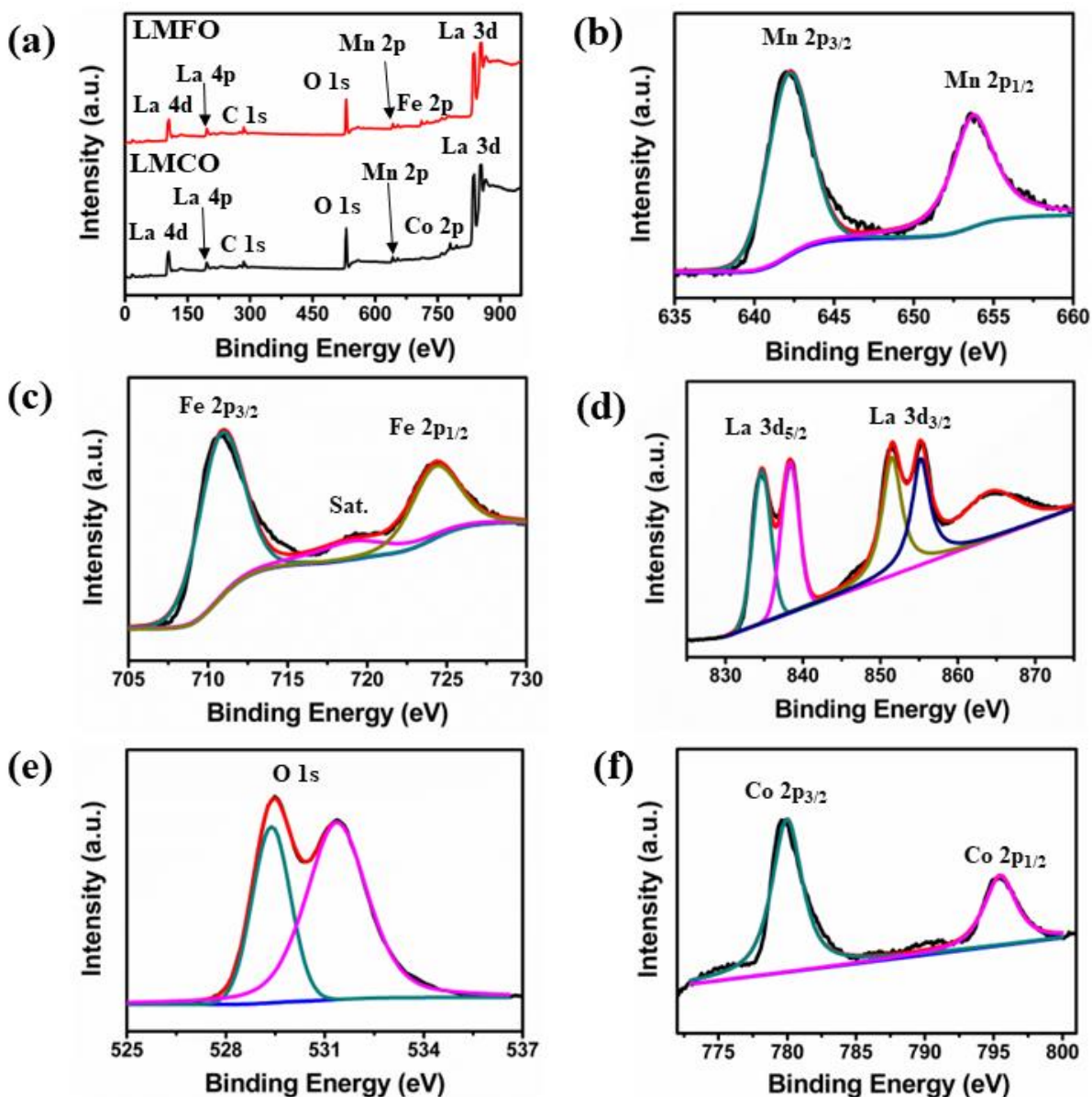


Figure 22: (a) XPS survey spectrum of LMCO and LMFO double perovskite, (b-e) deconvoluted peaks of Mn 2p, Fe 2p, La 3d, and O 1s of LMFO, and (f) deconvoluted peaks of Co 2p of LMCO double perovskite, respectively.

4.2.6. Simultaneous Thermogravimetry Analysis-(TGA/DSC)

For the thermal stability measurement, thermogravimetry (TGA) was simultaneously performed with a differential scanning calorimetry (DSC) study on both LMCO and LMFO samples, as shown in **Figure 23 (a, & b)**. The analysis is performed between the temperature range of 25°C-

900°C at a heating rate of 5°C/min. The TGA result shows that LMCO powder does not go through significant weight loss until a temperature of ~335°C. In the meantime, the DSC study also does not show any sharp exothermic/endothermic peak until a temperature of ~335°C, indicating no phase transformation between 0°C and 335°C [156]. This confirms the thermal stability up to 335°C. Beyond 335 °C, We can see an endothermic peak at 340 °C. At this temperature, Weight loss begins until the specimen undergoes ~1.5 % weight loss until 350 °C. After this temperature, no prominent exothermic/endothermic peak and only 0.8% weight loss until 900 °C shows the excellent stability of LMCO. LMFO shows a similar trend overall but only ~1 % weight loss until 350 °C. Beyond this temperature, only ~0.6 % weight loss until 900 °C. These results show that both LMCO and LMFO are stable. Still, in comparison, LMFO is the most stable, which indicates that these materials can work at high temperatures without any significant decomposition or phase change, which is essential for high-temperature energy storage applications.

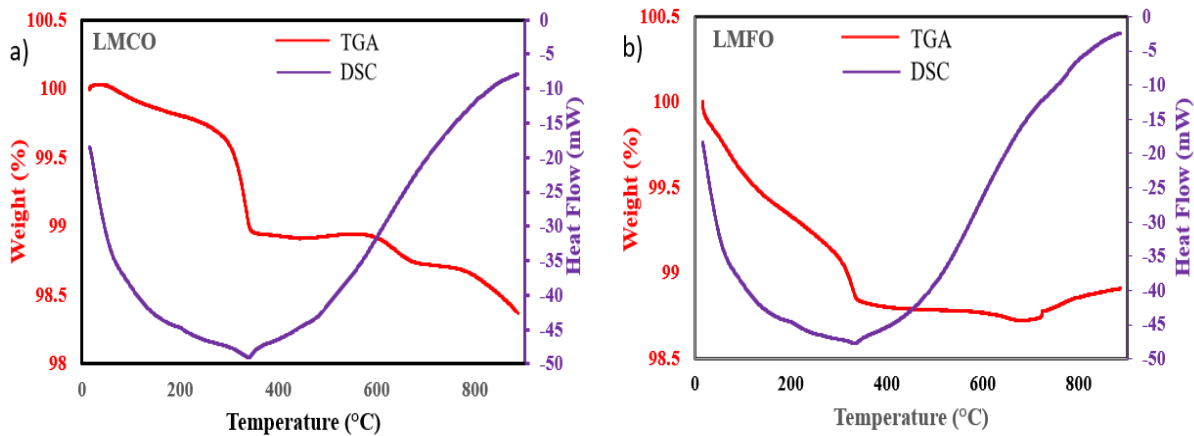
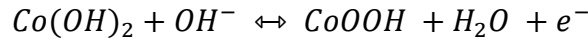


Figure 23. TGA/DSC of a) $\text{La}_2\text{MnCoO}_6$ and b) $\text{La}_2\text{MnFeO}_6$

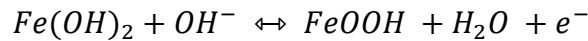
4.2.7. Electrochemical Performance

The electrochemical performance of prepared nanorods was initially investigated in the three-electrode setup using 1M KOH electrolyte. **Figure 24. (a, & b)** shows LMCO and LMFO CV curves at scan rates of 5, 10, 30, 50, and 100 mV/s in a potential window ranging from 0-0.55V and 0-0.5V, respectively. From the CV curves, we observed that cathodic and anodic scanning do not have symmetric and completely rectangular shapes. Meanwhile, we also noticed oxidation and reduction peaks, which amply demonstrate the developed material pseudocapacitive behavior. Charge may be held at the electrode surface via a faradic redox reaction. [81, 149]. These redox peaks may be ascribed to the faradic redox reactions of Co/Mn-O/Co/Mn-O-OH and Fe/Mn-O/Fe/Mn-O-OH [157]. Since the electrochemical measurement is done in 1M KOH, the redox reaction at the electrode surface is given by.

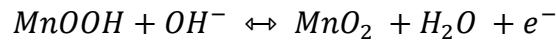
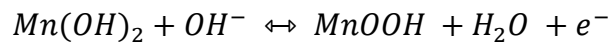
Redox reaction of the Co in 1M KOH;



Redox reaction for the Fe in 1M KOH;



And the reaction of Mn in 1M KOH;



At higher scan rates, surface effects produced the non-faradic double-layer growth. However, at lower scan rates, bulk diffusion predominates, which causes the redox peak current to rise. Faradic redox reactions occur at low scan rates because of the high response time [81, 158].

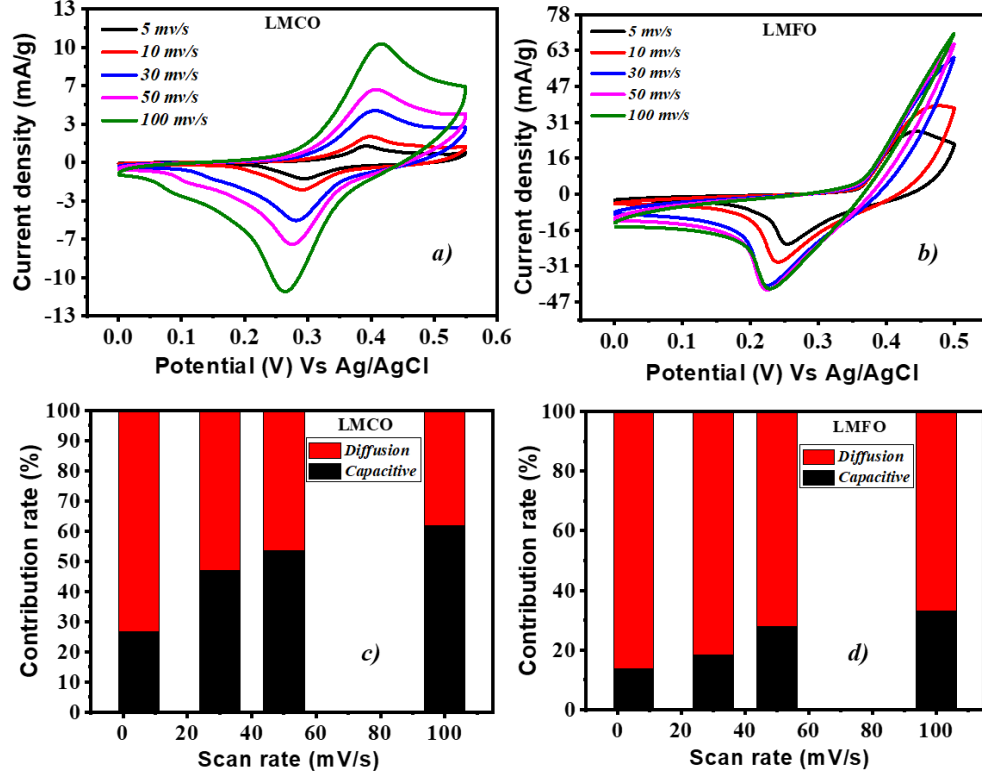


Figure 24. CV curves a) LMCO, b) LMFO and Capacitive and Diffusion contribution of c) LMCO, d) LMFO

The resultant specific capacitance arises due to diffusion-controlled and capacitive behavior. Diffusion control occurs when the electrochemical reaction is controlled by the diffusion of ions from the electrolyte to the electrode interface. Meanwhile, capacitive behavior occurs when the charge is stored through the electrostatic adsorption of ions at the electrode-electrolyte interface.

The contribution of diffusion and capacitive behavior can be separated by using Dunn's equation.

$$I = k_1 V + k_2 V^{1/2} \quad (17)$$

Where intercept of $V^{1/2}$ vs $1/V^{1/2}$. $k_1 V$ term related to capacitive and k_1 and k_2 are slope while $k_2 V^{1/2}$ term related to the diffusion-controlled behavior. **Table 8** presents the diffusion-controlled and the capacitive capacitance for varying scan rates.

The expression that relates them is.

$$\log i_v = \log a + b \cdot \log v \quad (18)$$

Where adaptable parameters ‘a’ and ‘b’, ‘a’ depends on electrode area, redox concentration species, and diffusion coefficient. The ‘b’ parameter may be evaluated using the slope of $\log i_v$ versus $\log v$. If $b = 1$, and the process is mainly controlled by diffusion. If $b = 0.5$, materials are capacitive. If the b value is low, it indicates diffusion-controlled behavior is dominant, While if the b value increases, it means capacitive behavior is dominant [159-161]. LMCO and LMFO have b values of 0.75 and 0.18, respectively, indicating that LMFO has more diffusion-controlled behavior than LMCO, as shown in **Figure 24 (c, & d)**.

Table 8. Capacitive and diffusion-controlled capacitance at different scan rates

Scan rate mV/s	% Diffusion LMCO	% Capacitive LMCO	% Diffusion LMFO	% Capacitive LMFO
5	73.34	26.65	86.41	13.58
10	66.05	33.94	81.80	18.19
30	52.90	47.09	71.19	27.80
50	46.53	53.46	66.78	33.21
100	38.09	61.90	58.71	41.28

GCD was also performed to analyze the electrochemical performance of LMCO and LMFO electrodes in potential window ranges 0-0.55 V and 0-0.5 V, respectively. **Figure 25 (a, & b)** shows the GCD scan for LMCO and LMFO electrodes. GCD curves showed non-linear behavior, indicating the pseudocapacitive nature of prepared electrodes [162, 163]. The Specific capacitance for LMCO and LMFO from the GCD curve is 333.8 and 880.5 Fg^{-1} , respectively @ current density of 2.5 Ag^{-1} . The discharge current density generally affects the specific capacitance [164]. In **Figure 25 (a, & b)**, discharge time declines with an increase in discharge current density. Hence, specific capacitance drops due to reduced storage capacities, such as diffusion of ions in the

electrolyte and redox reactions at the electrode/electrolyte interface. The higher capacitance value in LMFO may be ascribed to its suitable structure and higher theoretical surface area, which facilitates the electrolyte's entry into the material. Furthermore, cyclic voltammetry analysis suggests that the rise in diffusive contribution in LMFO could be the cause of this capacitance increase.

Two essential metrics used to describe how energy storage devices behave are the specific energy and the specific power. In addition to the capacitance, LMFO yields high specific energy and power values. For LMCO, energy density is lower than that of LMFO. Energy and Power density values for LMFO are 30.5 Wh/Kg and 625 W/Kg, respectively, at the current density of 2.5 A/g. Energy and power density values for LMCO are 14.0 Wh/Kg and 687.5 W/Kg, respectively. **Tables (9, & 10)** show the electrochemical parameters of the LMFO and LMCO electrodes, respectively.

Table 9. The electrochemical parameters for $\text{La}_2\text{MnFeO}_6$

Current density (A/g)	Specific Capacitance (F/g)	Power density (W/Kg)	Energy density (Wh/Kg)
2.5	880.5	625	30.5
3	852.1	750	29.5
3.5	840.4	875	29.1
4	824.2	1000	28.6

Table 10. The electrochemical parameters for $\text{La}_2\text{MnCoO}_6$

Current density (A/g)	Specific Capacitance (F/g)	Power density (W/Kg)	Energy density (Wh/Kg)

2.5	333.8	687.5	14.0
3	117.8	825	5
3.5	108.1	962.5	4.5
4	87.2	1100	3.6

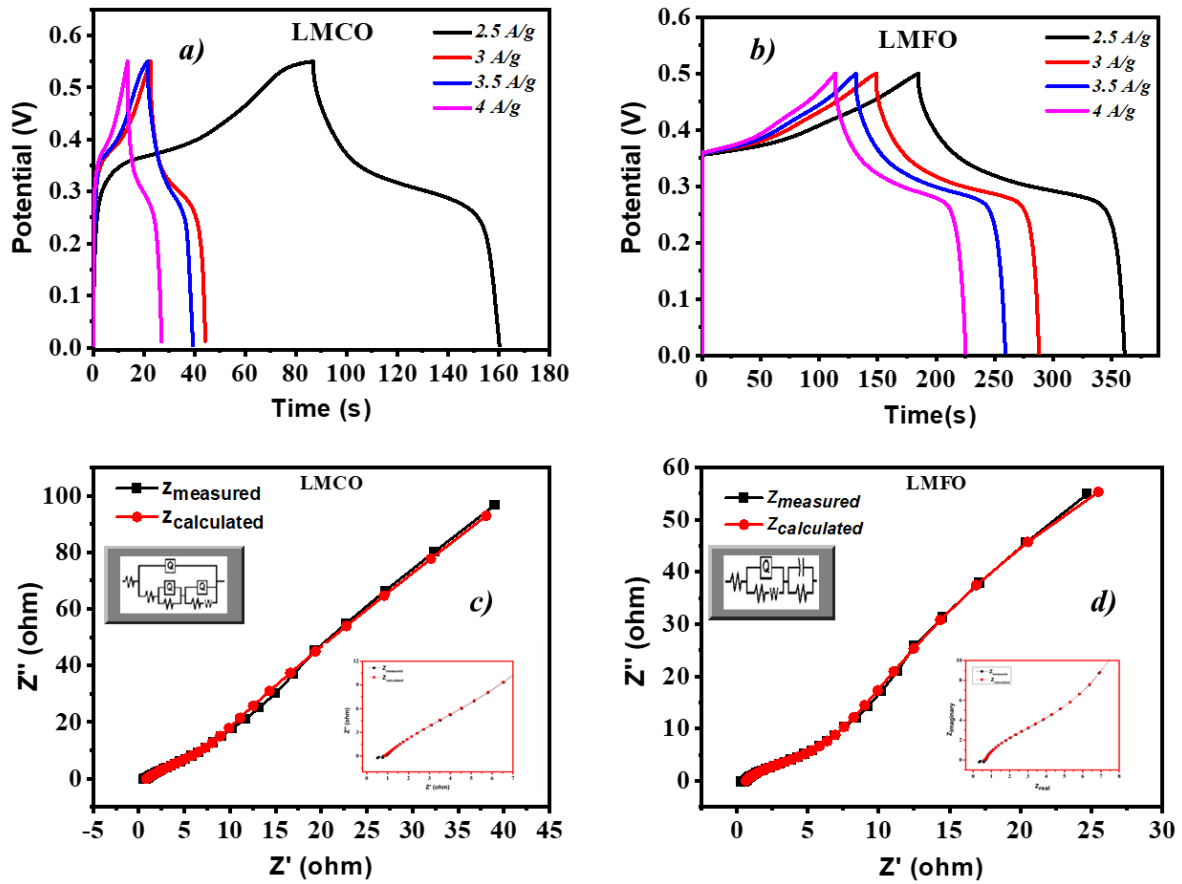


Figure 25. GCD curves of a) LMCO, & b) LMFO, Nyquist Plot of c) LMCO, & d) LMFO

Figure 26 a), shows the Nyquist plot of LMCO and LMFO nanorods. In the frequency range of 0.1 Hz-100 MHz, EIS tests were done. EIS evaluates the electrode material's electrochemical reaction kinetics and conductivity [165]. The intercept at the X-axis in the Nyquist plot represents the ionic resistance/ series resistance (R_s) that electrolytes offer during the movement of ions at the electrode-electrolyte interface. The diameter of the semicircle tells about the charge transfer

resistance (R_{ct}). Meanwhile, the slope of the inclined line is related to diffusive impedance. The obtained plot was also fitted using Zsimpwin software, as shown in **Figure 25 (c & d)**. The measured R_s and R_{ct} values are shown in **Table 11**. **Figure 26a** shows a comparative Nyquist plot for both LMCO and LMFO nanorods, while **Figure 26b** shows a zoomed view of the Nyquist plot of LMCO and LMFO.

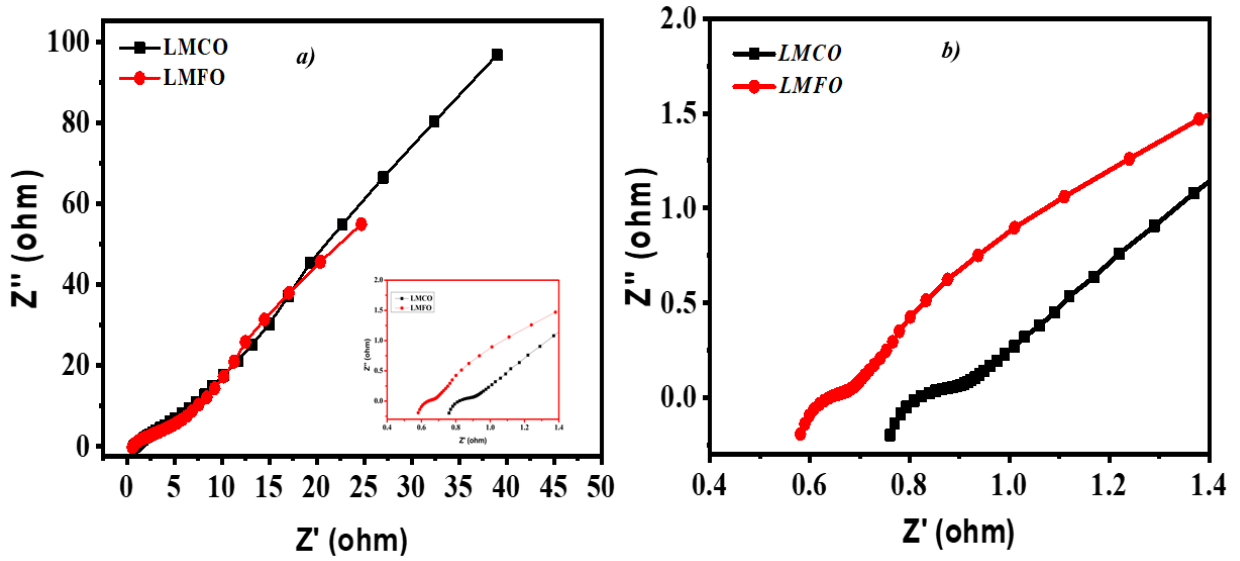


Figure 26. Nyquist Plot of LMCO and LMFO, b) Zoomed EIS of LMCO and LMFO,

We observed that both the series and charge transfer resistance of LMCO are higher than those of LMFO, which is why LMFO has a higher capacitance and charge transfer rate. Also, LMFO showed better electrochemical performance than LMCO, which might be owing to its greater electrical conductivity and low band gap value. Also, from the FESEM, we observed that the LMFO sample mostly has mesopores, which facilitate the charge transfer process and indicate that it has more surface area. Thus, high electrical conductivity and better surface area are essential for electrochemical supercapacitor electrodes. LMFO showed better electrochemical performance than LMCO as a supercapacitor electrode material.

Table 11. The measured R_s and R_{ct} for LMCO and LMFO

Sample	Series resistance (R_s) (Ω)	Charge transfer resistance (R_{ct}) (Ω)
LMCO	0.76	0.28
LMFO	0.58	0.25

4.3. Synthesis and Characterizations of Novel 2D Ti_3C_2 -MXene/ $\text{La}_2\text{MnFeO}_6$ -double perovskite nanocomposite for High-Performance Supercapacitor Applications

4.3.1. X-Ray Diffraction:

X-ray diffraction (XRD) studies were employed to examine Ti_3C_2 -MXene and Ti_3C_2 -MXene/ $\text{La}_2\text{MnFeO}_6$ nanocomposite. **Figure 27.** shows characteristics of X-ray peaks at ranges from $2\theta = (5 \text{ to } 80)^\circ$. The sharp diffracted 2θ peaks for Ti_3C_2 -MXene were located at 10° , 18° , 27° , and 61° corresponding to the planes (002), (004), (006), and (110) respectively. The rest of the peaks at 23° , 32° , 40° , 46° , 57° , 69° , and 77° correspond to planes (110), (200), (202), (220), (312), (224), and (240) which belong to $\text{La}_2\text{MnFeO}_6$ that indicates the synthesis of stable composite. The small changes in the position of the peaks and the possible broadening indicate good structural compatibility between the two materials. This compatibility plays an essential role in the mechanical stability of the composite during continuous cyclical charge and discharge, one of the conditions for stable long-term operation of supercapacitor electrodes.

This data also confirms the successful synthesis of the Ti_3C_2 -MXene/ $\text{La}_2\text{MnFeO}_6$ nanocomposite. The minor peak shift in the nanocomposite represents the successful integration of $\text{La}_2\text{MnFeO}_6$ into MXene as well as variations in the lattice parameters in the composite crystal structure [166].

In the formation of Ti_3C_2 -MXene composite with perovskite material $\text{La}_2\text{MnFeO}_6$, the crystalline size is reduced from 11nm to 6nm, this contradiction between the MXene phase and perovskite phase likely causes lattice mismatch, which causes strain at interfaces to limit crystalline growth of MXene.

Smaller crystalline sizes can also improve some attributes of a material like surface area, which is usually desired for uses such as supercapacitors. In these scenarios, it has been suggested that

smaller crystalline domains may lead to enhanced electrochemical performance due to more active sites being available for ion storage or redox reactions.

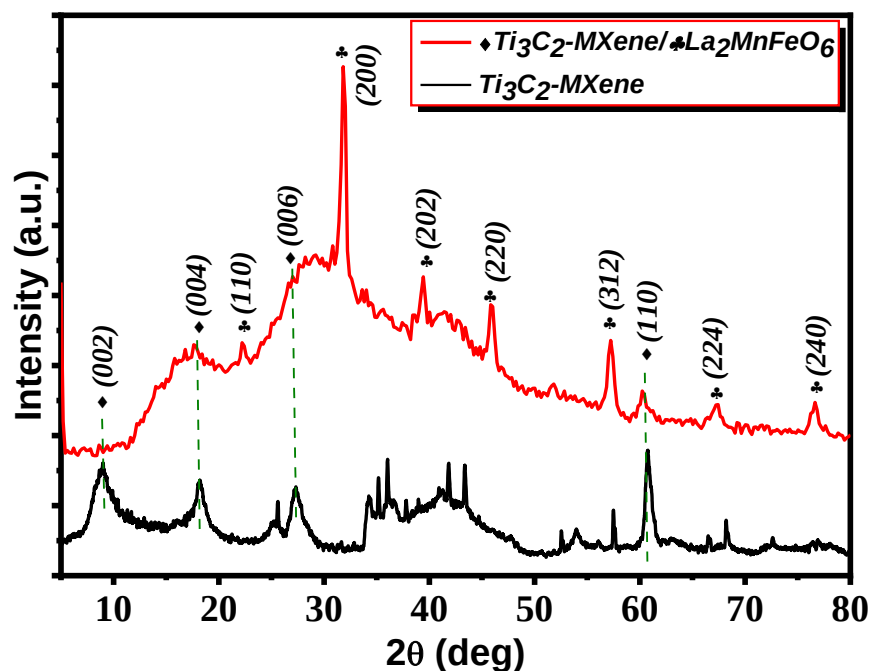
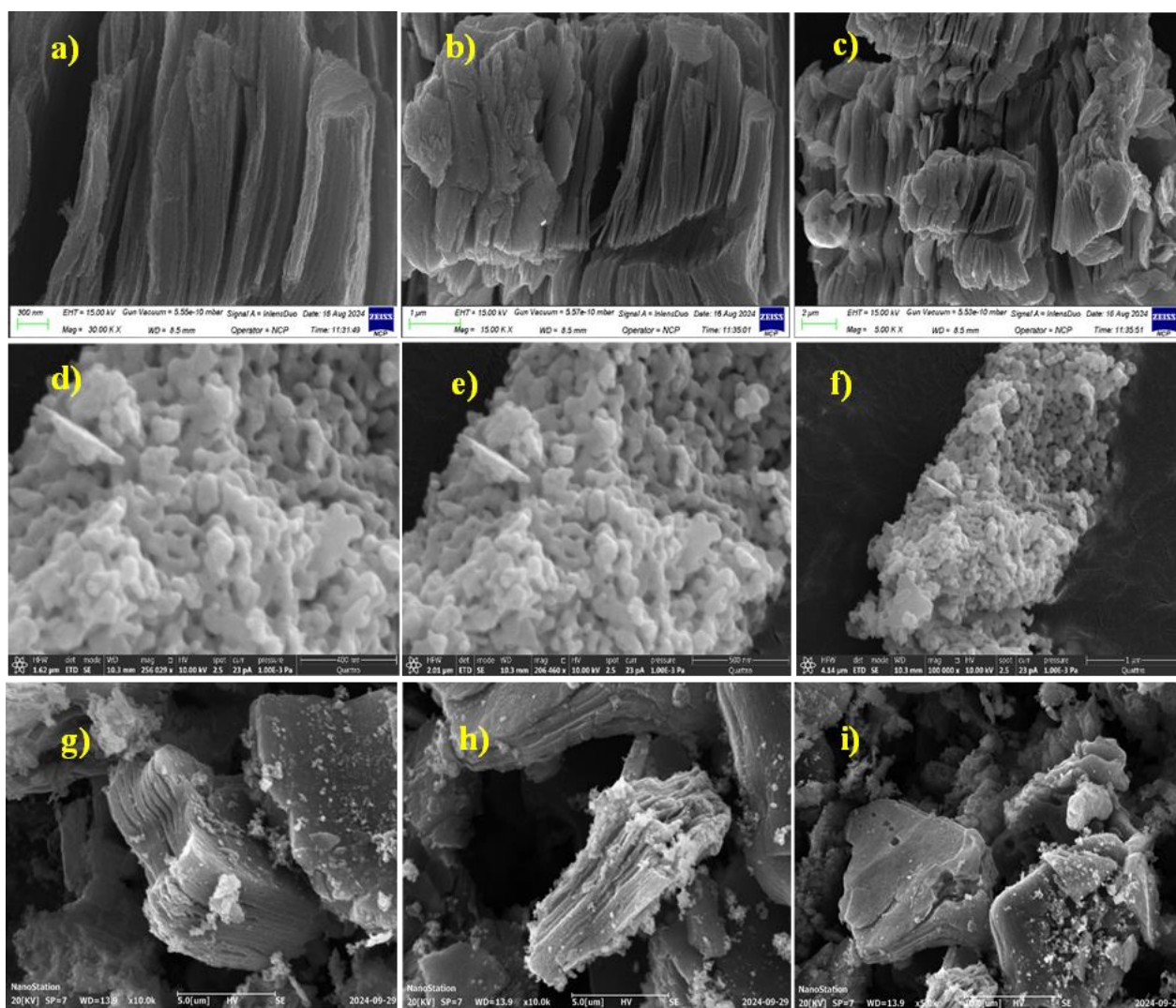


Figure 27. XRD pattern of $\text{Ti}_3\text{C}_2\text{-MXene}$ & $\text{Ti}_3\text{C}_2\text{-MXene}/\text{La}_2\text{MnFeO}_6$ nanocomposite

4.3.2. Scanning Electron Microscope:

The microstructures of $\text{Ti}_3\text{C}_2\text{-MXene}$ and $\text{Ti}_3\text{C}_2\text{-MXene}/\text{La}_2\text{MnFeO}_6$ nanocomposite were investigated by Scanning Electron Microscopy (SEM). **Figure 28 (a, b & c)** are the images of pure $\text{Ti}_3\text{C}_2\text{-MXene}$, which show the sheet-like structure of MXene. It can also be seen that the sheets of $\text{Ti}_3\text{C}_2\text{-MXene}$ are well-separated which confirms the successful delamination of multi-layer $\text{Ti}_3\text{C}_2\text{-MXene}$ to monolayer $\text{Ti}_3\text{C}_2\text{-MXene}$. **Figure 28 (d, e & f)** shows SEM micrographs of $\text{La}_2\text{MnFeO}_6$. **Figure 28 (g, h & i)** represents the composite $\text{Ti}_3\text{C}_2\text{-MXene}/\text{La}_2\text{MnFeO}_6$, these images show a complex morphology, where $\text{La}_2\text{MnFeO}_6$ is well distributed on the surface of MXene as well as between the layers of MXene. This integrated architecture is beneficial for

supercapacitors because the large surface area of $\text{La}_2\text{MnFeO}_6$ could couple with the conductive layers of MXene, leading to improved charge storage and more efficient ion transport pathways. In addition, the $\text{La}_2\text{MnFeO}_6$ particles also increase the surface roughness to provide more active sites involved in the electrochemical reaction mechanism which can enhance the overall capacitance of the supercapacitor. The associated elemental mapping (**Figure 28g.**) depicts the uniform distribution of Ti, C, La, Mn, Fe, and O, while no traces of Al can be seen, which confirms the successful etching. Ideally, MXene should have no or minimal residual Al to fulfill the complete transformation from the MAX phase to MXene and the full delamination process.



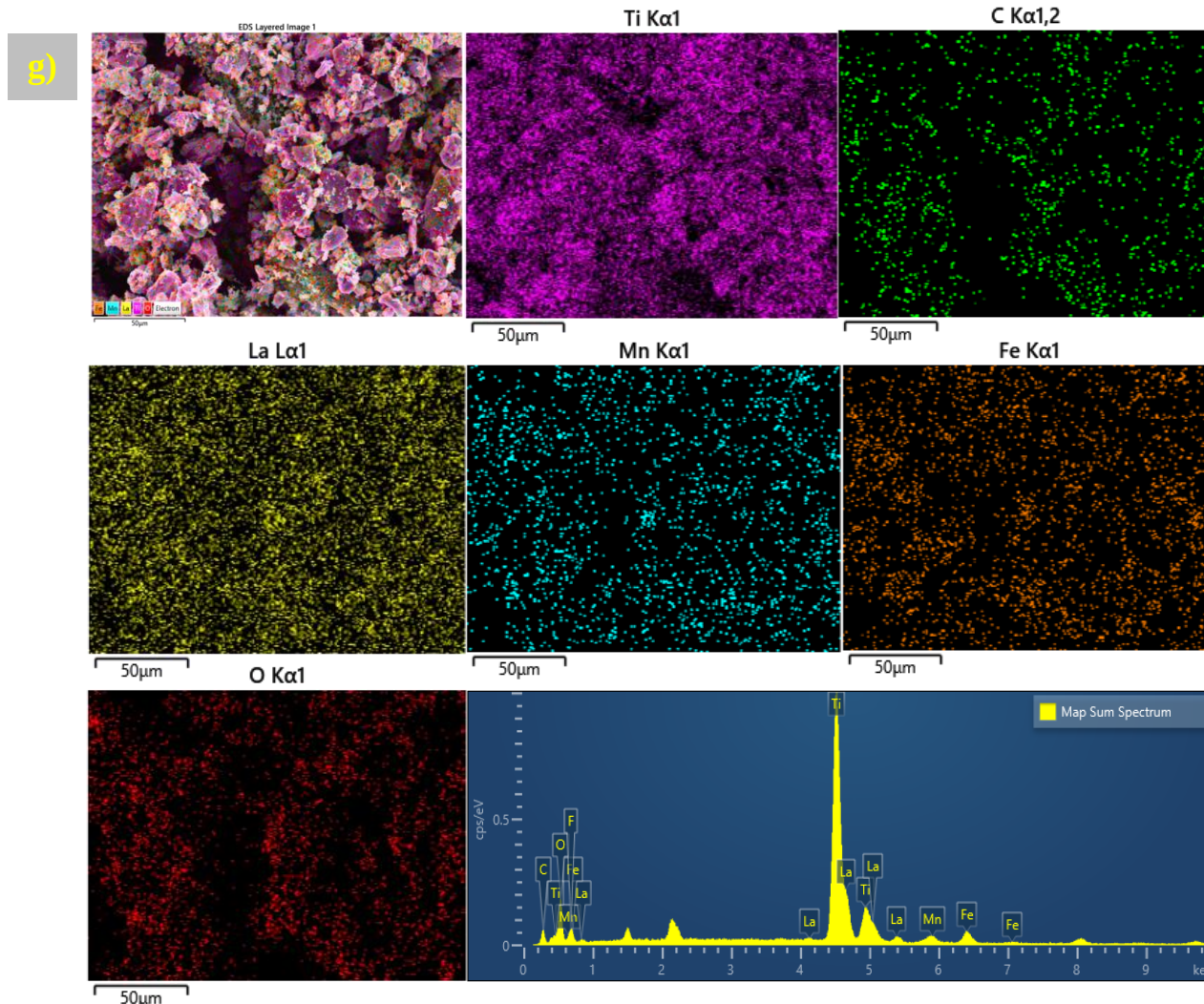


Figure 28. SEM micrographs of Ti_3C_2 -MXene (a, b & c), $\text{La}_2\text{MnFeO}_6$ (d, e, & f), Ti_3C_2 -MXene/ $\text{La}_2\text{MnFeO}_6$ nanocomposite (g, h, & i). EDX and mapping of detected Titanium (Ti), Carbon (C) Lanthanum (La), Manganese (Mn), Iron (Fe), and Oxygen (O) in MXene/ $\text{La}_2\text{MnFeO}_6$ nanocomposite (j)

4.3.3. X-ray photoelectron spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) was employed to examine the oxidation states, composition, and chemical environment of the synthesized MXene/LMFO nanostructures, respectively, as shown in Figures 1 and 2. The survey spectrum of the synthesized MXene/LMFO nanostructures is presented in Figure 1. The survey spectrum shows the elemental presence of Lanthanum (La), Manganese (Mn), Iron (Fe), Carbon (C), Titanium (Ti), and Oxygen (O) in the

synthesized materials. Figure 2 (a-f) displays the deconvoluted peaks of each element in the synthesized MXene/LMFO nanostructures.

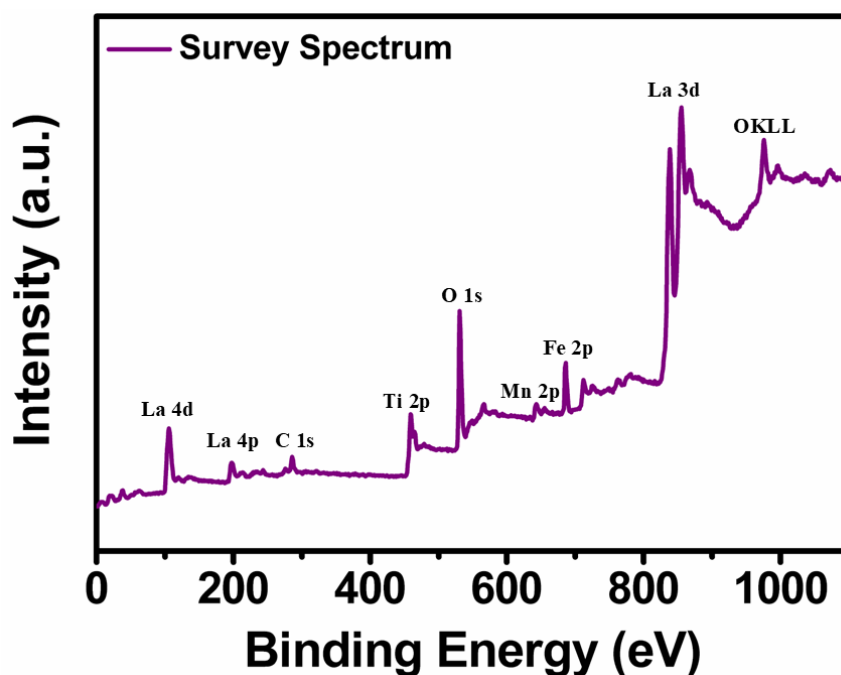


Figure 29. XPS survey spectrum of synthesized $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite.

Figure 30 (a-f) depicts the deconvoluted peaks of each element present in $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite. In **Figure 30a**, two significant peaks for La 3d were detected at the binding energies of 833.69 eV/837.53 and 850.30 eV/854.60 eV, respectively, corresponding to La $3d_{5/2}$ and La $3d_{3/2}$, demonstrating La^{3+} oxidation state in $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite [153]. Additionally, two distinct peaks at binding energies of 642.95 eV and 654.22 eV were observed due to spin-orbit coupling attributed to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, suggesting the Mn^{3+} oxidation state (**Figure 30b**) [167]. Likewise, we observed two prominent peaks for Fe 2p in Figure 2c at lower and higher binding energies, 712.06 eV and 725.84 eV, assigned to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ along with a satellite peak at a binding energy of 718.59 eV respectively, confirming the presence of Fe^{3+} oxidation state [167]. The C 1s deconvoluted spectrum of $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ shows the binding energies of 282.39 eV, 285.62 eV, and

287.33 eV, confirming the presence of presence of C-Ti, C-C/C=C, and C-O in $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite, as shown in **Figure 30d** [168]. **Figure 30e** displays the two prominent peaks in the Ti 2p spectra, located at 459.50 eV and 465 eV, respectively, which are associated with Ti $2p_{3/2}$ and Ti $2p_{1/2}$ due to the spin-orbit coupling. The other indicative peak at a binding energy of 454.91 eV suggests the Ti-O band in the $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite [169]. Furthermore, the O 1s spectra were deconvoluted into two three distinct peaks confirming the O^{2-} oxidation states with binding energies of 530.55 eV, 531.69 eV, and 532.91 eV corresponding to carbon-titanium-oxygen bond (C-Ti-O,) metal-oxygen bond (M-O) and carbon-titanium-hydroxide bond (C-Ti-OH) for absorbed OH oxygen species in $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposites, respectively (as shown in **Figure 30f.**) [168].

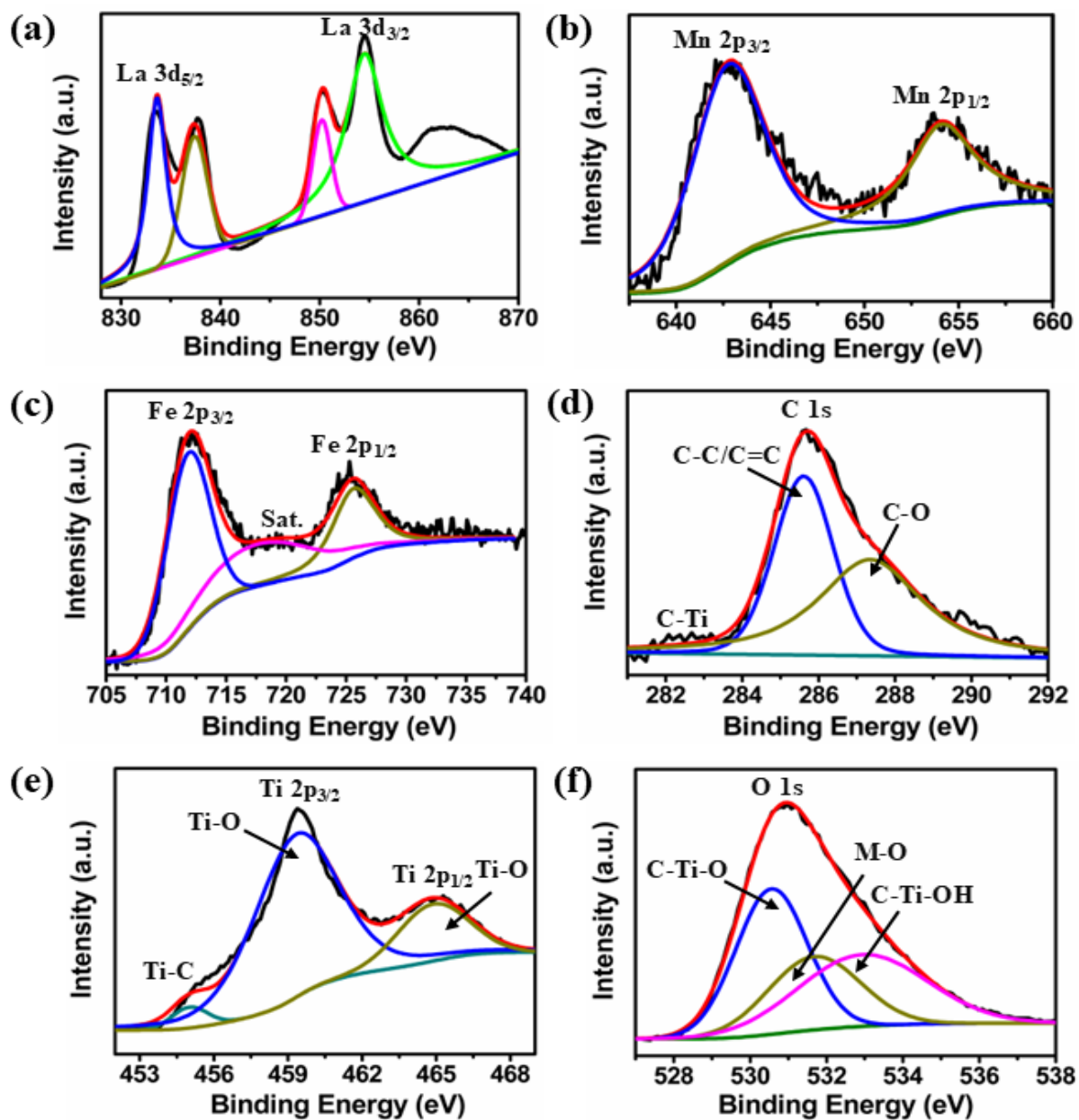


Figure 30. XPS deconvoluted spectrum of $\text{Ti}_3\text{C}_2\text{-Mxene/La}_2\text{MnFeO}_6$ nanocomposite. (a-f) deconvoluted peaks of La 3d, Mn 2p, Fe 2p, C 1s, Ti 2p, and O 1s, respectively.

4.3.4. Three electrodes:

Three electrode cell electrochemical performances were determined prior to the Asymmetric cell fabrication. CV and GCD analysis were performed to evaluate the comparison between $\text{La}_2\text{MnFeO}_6$ and $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$. $\text{La}_2\text{MnFeO}_6$ double perovskites and $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite electrochemical performances in CV curves shown in **figure 31 (a & b)** which indicates that the material composition has a significant effect on their redox activity as well as charge storage capability. Cyclic voltammogram scans performed on $\text{La}_2\text{MnFeO}_6$ electrode material exhibited a quasi-rectangular shape and redox peaks, suggesting that the studied samples possessed pseudocapacitive performance. As expected, the maximum value of redox peak intensity and area of CV curve of the $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite electrode are much larger than that of $\text{La}_2\text{MnFeO}_6$ double perovskite electrodes due to high oxygen vacancy in $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite and high surface area property for charge storage inside Ti_3C_2 -MXene. The weak redox peaks of bare $\text{La}_2\text{MnFeO}_6$ can be attributed to limited charge transfer and reversible reduction. The oxidation peak gradually shifts to a more positive potential region while the reduction peak moves to the lower potential region with an increasing scan rate, which can be ascribed to the internal diffusion resistance developed in electrode material [38, 60, 170].

The redox peaks arise from reversible Mn and Fe ion transitions intrinsic to the double perovskite structure. The curves are symmetric, implying good reversibility for all charge-discharge processes. The CV curves of $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ all exhibited better rectangular at lower scan rates, and had a remarkable enhancement in redox peaks compared to those of the pristine $\text{La}_2\text{MnFeO}_6$. This improvement comes from the synergistic effect of Ti_3C_2 MXene in terms of two aspects: 1) creating a conductive network for fast charge transfer and; 2) providing extra active sites to increase more faradaic reactions.

The composite material exhibits enhanced capacitive behavior at high scan rates for utilization at higher-rate applications. The high conductivity of MXenes leads to the enhanced rate capability, mitigating ion diffusion limitations. The CV curves of the $\text{La}_2\text{MnFeO}_6$ double perovskites and Ti_3C_2 -based/ $\text{La}_2\text{MnFeO}_6$ composite depict different electrochemical properties due to material composition affecting redox activity, and charge storage capacity. The current density variation of the aforementioned scan rates (3 mV s^{-1} to 50 mV s^{-1}) is displayed in this case an incremental significantly redox peaks with respect to their peak currents, indicating good accessibility and electrode kinetics for ions.

GCD is the most suitable among CV and GCD for the determination of the specific capacity of the electrode material [61, 62]. **Figure 31** (c & d) shows GCD profiles for $\text{La}_2\text{MnFeO}_6$ double perovskites and Ti_3C_2 -based/ $\text{La}_2\text{MnFeO}_6$ composite at various current densities (0.5 to 2 A g^{-1}) respectively. As demonstrated in **Figure 31** (c & d) this indicates that the charge curves have no mirror symmetry when compared to their respective discharge ones across the whole potential window for these materials. Such asymmetry comes from electrode surface redox reaction [140]. Compared with the $\text{La}_2\text{MnFeO}_6$ electrode, the Ti_3C_2 -based/ $\text{La}_2\text{MnFeO}_6$ exhibits longer discharging time at the same current density, suggesting that higher capacity of Ti_3C_2 -based/ $\text{La}_2\text{MnFeO}_6$ at all current densities. The enhancement activity of Ti_3C_2 -based/ $\text{La}_2\text{MnFeO}_6$ is due to the higher concentration of oxygen vacancies and the synergistic redox effects in its structure. Such behavior may be ascribed to the incorporation of MXenes, which accelerate ion transports and increase specific surface areas for active sites. Furthermore, the low agglomeration of Ti_3C_2 -based/ $\text{La}_2\text{MnFeO}_6$ can accelerate ion transport compared to pristine $\text{La}_2\text{MnFeO}_6$ provides more active sites for the electrode-electrolyte interaction. As shown in the GCD curves, the IR drop decreases with decreasing current density. This is because, at these lower current

densities, there are longer durations available for ion exchange processes. The GCD results corresponded well with the CV data, and showed much better performance of $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ composite than pristine $\text{La}_2\text{MnFeO}_6$ in specific capacitance, rate capability, and energy storage efficiency. The synergy of MXene double perovskite results in higher electrochemical performance.

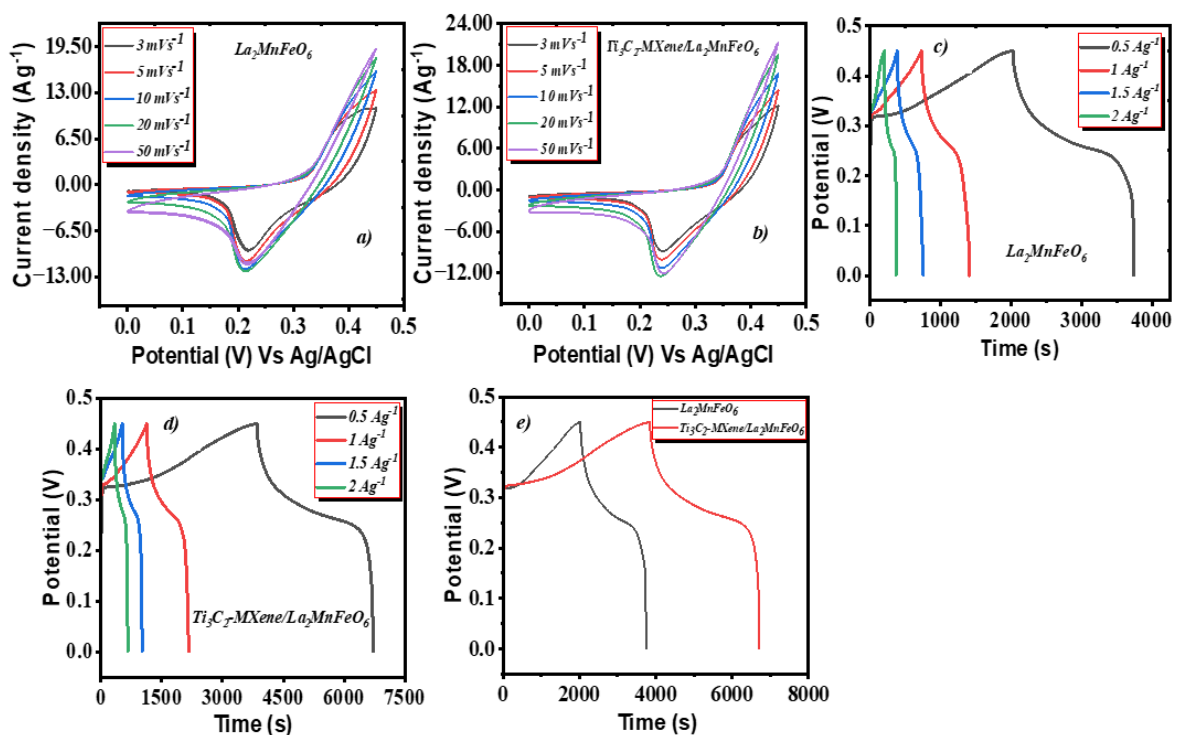


Figure 31 Cyclic voltammetry (a, & b), Galvanostatic charge-discharge at various current densities (c & d), of $\text{La}_2\text{MnFeO}_6$ and $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite respectively. Comparative GCD curve at 0.5 Ag^{-1} (e)

4.3.5. Two electrode device configuration:

An asymmetrical device was set up to evaluate composite electrode performance, where one electrode was $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ composite, and the other was Activated Carbon sandwiched by Glass fiber as a separator. Electrochemical Performance Characteristic Curves were used to characterize the performance of devices in 1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide as an electrolyte under a potential range of 0-2.5V. Scan rate dependence for the two-electrode supercapacitor device in (a) and (b).

The device using $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite displays an almost rectangular CV curve with area increases as the scan speed increases and the shape stays nearly the same, which shows excellent rate performance. In addition, the GCD curve over various current densities is shown in **Figure 32(b)** (between 0.2-1 Ag^{-1}). The C_{sp} from GCD can be calculated by using the relation,

$$C_{sp} = \frac{I\Delta t}{m\Delta V} \quad (19)$$

In the above equation, I is the constant current, m is the total loading of active materials, Δt is the discharging time, and ΔV is the potential window. The device electrochemical parameters of the $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6$ nanocomposite calculated are presented in **Table 12**.

The energy (E_d) and power density (P_d) of a fabricated device was calculated using the following relations.

$$E_d = \frac{1}{2} C_{sp} \Delta V^2 \quad (20)$$

$$P_d = \frac{E_d}{\Delta t} \quad (21)$$

Where C_{sp} is the specific capacitance calculated from the GCD, ΔV is the potential difference and Δt is discharge time.

The Ragone plot indicates the good rate capability of this Asymmetric device. The device provides high energy densities of 81.25 Wh/kg at a power density of 300 W/kg at a current density of 0.2A/g.

Table 12. Electrochemical parameters of $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6//\text{AC}$ based device

Current density (A/g)	Specific capacitance (F/g)	Power density (W/kg)	Energy density (Wh/kg)
0.2	65.00	300	81.25
0.4	49.33	600	61.66
0.6	34.6	900	43.25
0.8	24.53	1200	30.66
1	20.00	1500	25

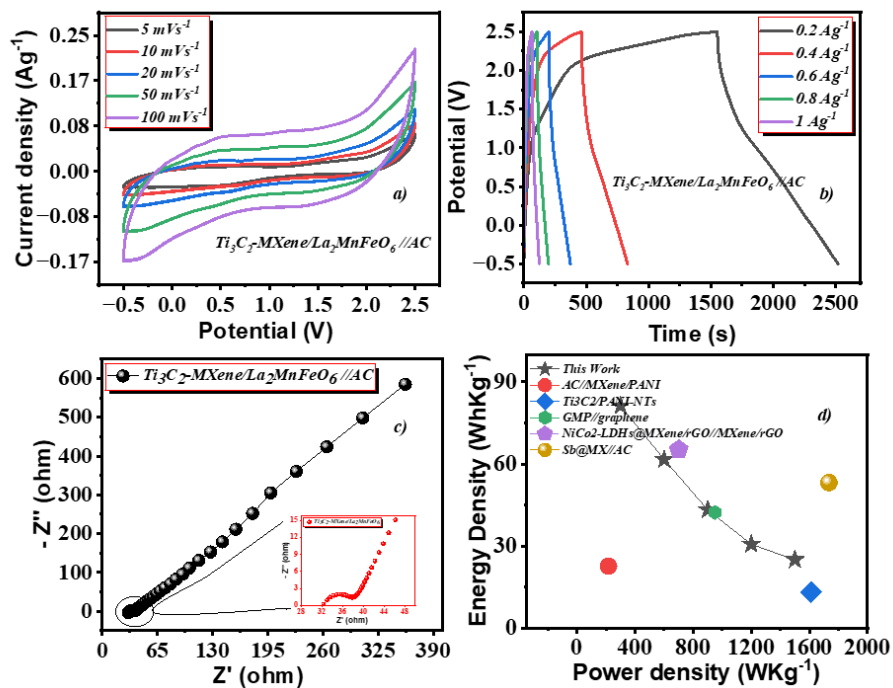


Figure 32 Cyclic voltammetry (a), Galvanostatic charge-discharge at various current densities (b), Electrochemical impedance spectroscopy (c), and Ragone plot (d) for $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6//\text{AC}$ based device

Constant current charge-discharge tests of the fabricated supercapacitor device were conducted over 1700 cycles to evaluate the cyclic stability. Surprisingly, this device demonstrated excellent cycling stability with 95.7 % of capacitance retention after 7000 cycles, and a high coulombic efficiency of 96.2% (Figure 33a.).

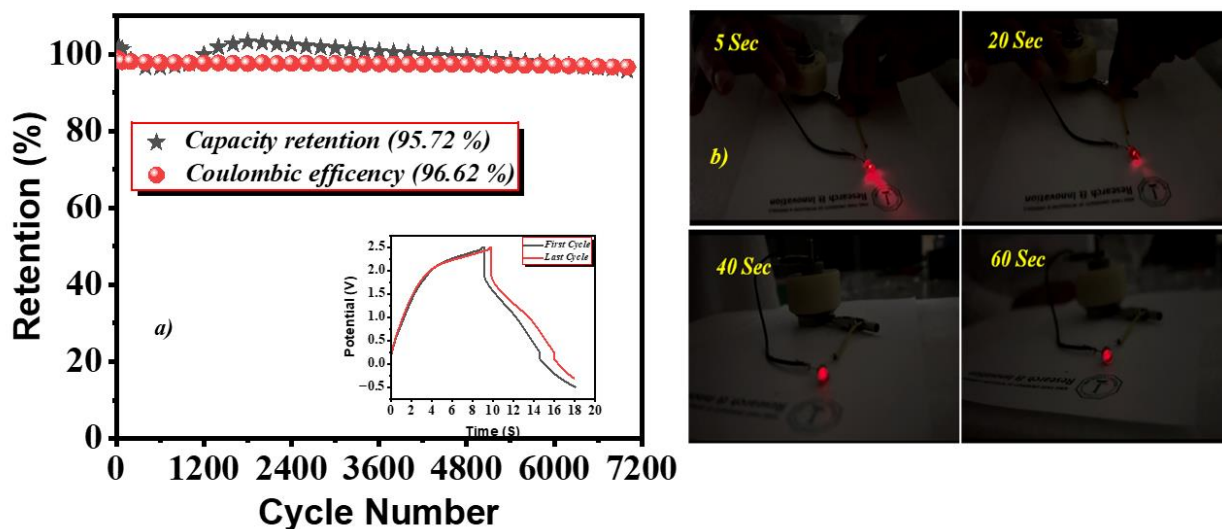


Figure 33 Capacity retention and Coulombic efficiency of $\text{Ti}_3\text{C}_2/\text{La}_2\text{MnFeO}_6//\text{AC}$ based device

In addition, to practically prove the functionality of the device, an LED was powered using the same device, with multiple snapshots captured at different time intervals as shown in **Figure 33b**. These results highlight the outstanding stability and potential of the device for real-world energy storage applications.

CHAPTER 5

Conclusions and Future work

Research in high-performance supercapacitors is important due to the global market need for

efficient, sustainable and scalable energy storage technologies. This thesis has presented the successful fabrication & detailed characterization of perovskite oxide-based hybrid supercapacitors. The systematic study suggests new insights into synthesizing materials, structure characterization and electrochemical performance optimization of electrode materials used for energy storage applications.

The objective of this research was to contribute to the synthesis and characterization of perovskite oxide-based electrode materials in, particular: 1) Mn-Ru co-doped LaNiO_3 ; 2) $\text{La}_2\text{MnCoO}_6$; 3) $\text{La}_2\text{MnFeO}_6$ and $\text{La}_2\text{MnFeO}_6/\text{Ti}_3\text{C}_2\text{-MXene}$ nanocomposites. The highly promising features of perovskite oxides such as tunable bandgap, high stability and excellent redox activity suggest them to be a new generation of supercapacitance materials. The synthesis of these materials was performed with processes aimed to optimize their crystallinity, morphology, and surface area, all key properties needed for good electrochemical performance.

The synthesized materials were characterized by their physical and chemical properties using advanced characterization techniques. XRD and XPS analyses revealed the crystalline structure and confirmation of successful doping of transition metals into the host compound, While FE-SEM analysis provided surface morphology and FTIR provided functional group information. The TGA studies confirmed that the thermal stability of these materials was appropriate for high-temperature conditions too. $\text{Ti}_3\text{C}_2\text{-MXene}$ was combined with $\text{La}_2\text{MnFeO}_6$ double perovskite for improved conductivity, surface area, and ion accessibility through synergistic effects of hybrid materials which can aid supercapacitor performance.

The significance of the synthesized materials in supercapacitor applications was revealed by using various electrochemical techniques. The CV exhibited good redox activity and capacitive behavior, while the GCD showed high specific capacitance values. Ruthenium doping increased

the electronic conductivity and charge storage capability of pure LaNiO_3 perovskite material. The Mn-Ru co-doped LaNiO_3 electrode demonstrated a significantly increased specific capacitance. This work revealed the important role of hybridization in tackling energy-power tradeoffs in supercapacitors, as evidenced by superior energy and power densities for the $\text{La}_2\text{MnFeO}_6/\text{Ti}_3\text{C}_2$ -MXene nanocomposite.

The fabrication of asymmetric devices by coupling the perovskite oxide materials with commercially available activated carbon further proved their potential for practical applicability. The device demonstrated an energy density of 82.5 Wh/kg and a power density of 1350 W/kg with superb cycle stability within the potential window of 0-2.5 V. The findings highlight the importance of perovskite oxides for high-performance supercapacitor applications, overcoming key limitations in the field.

This rich knowledge of synthesis, doping as well as hybridization with MXenes will open a gate for next-generation supercapacitors. Further, the integration of these materials into final device configurations highlights their up-scalability and usability in practical devices.

Even though the results are promising, challenges and opportunities for future research services still exist. The long-term stability of the devices results in rapid environmental switching, opening the door to further work. Finally, more attention should be paid to the scalability of synthesis processes and their economic usage of rare transition metals (e.g.: Ru). The development of sustainable synthesis methods by the requirements of sustainable development goals should also be explored along with optimizing the interface between electrode and electrolyte in further research.

Finally, this thesis shows that Mn-Ru co-doped LaNiO_3 , LaMnCoO_6 , LaMnFeO_6 , and

$\text{La}_2\text{MnFeO}_6/\text{Ti}_3\text{C}_2\text{-MXene}$ nanocomposites have a great future for supercapacitor uses. These innovative materials are simple to synthesize and have never been attempted before in the research and development of energy storage systems. This work builds upon the synthesis and use of perovskite oxides — contributing new knowledge to these frameworks for future innovations towards satisfying global energy demands in a sustainable manner.

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PUBLICATIONS

Journal Publications

1. **Ahmar Ali**, Mohammed A. Gondal, Javed A. Khan, Munerah A. Almessiere, Abduhadi Baykal, Sultan Ahmed “Synthesis and Investigation of Electrochemical Performance of La_2MnXO_6 (X=Co, Fe) Double Perovskites for Supercapacitors Applications” (Under review).
2. **Ahmar Ali**, Mohammed A. Gondal, A. Majeed, Mujahid Mustaqeem, Khansa Masood, Munerah A. Almessiere, Abduhadi Baykal, “Tuning Electrochemical Behavior of the LaNiO_3 electrode via Mn-Ru co-doping for Enhanced Energy Storage Performance” (Submitted).
3. **Ahmar Ali**, Mohammed A. Gondal, A. Majeed, Mujahid Mustaqeem, Khansa Masood Synthesis and Characterizations of Novel 2D Ti_3C_2 -MXene/ $\text{La}_2\text{MnFeO}_6$ -double perovskite nanocomposite for High-Performance Supercapacitor Applications (Manuscript under preparation)
4. S. Ahmed; Mohammed A. Gondal, J. A. Khan; Munerah A. Almessiere; A. Baykal; **Ahmar Ali**; A. S. Alzahrani “Tuning the Composition of Manganese Cobaltite Spinel with Tungsten for Enhanced Energy Storage Performance” Nano-Structures & Nano-Objects (2024)

Conference Papers/Presentations

1. Poster presentation at ‘International Conference on Research Advancements in Chemistry 2024 (ICRA-C 2024), organized by the Department of Chemistry, National University of Sciences and Technology (NUST) Islamabad-21st – 23rd Aug 2024.
2. Poster Presentation in Three Days 3rd International Conference on Physical Sciences and Engineering (ICPSE-2023), organized by Khwaja Fareed University of Engineering & Information Technology (KFUEIT), Punjab Pakistan – May 16-18, 2023.