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Article

Microstructure and Electrochemical Properties of Pure and Vanadium-Doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanoflakes for High Performance Supercapacitors

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Abstract: Nanostructured binary metal oxides have demonstrated the potential for increased electrochemical performance due to their structural stability, electronic conductivity, and various oxidation states. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was successfully synthesized via a hydrothermal procedure with different reaction periods (12, 18, and 24 h), followed by microstructural and supercapacitive characteristics. The XRD and XPS studies verifies the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ pure phase after 24 h (LTO@12) of reaction time with computed average crystallite size of 13 nm. FESEM and HRTEM images reveal nanoflake surface morphology. Cyclic voltammetry, galvanostatic charge discharge, and electrochemical impedance spectroscopy were used to investigate the electrochemical performance of LTO@24 electrode material. The LTO@24 nanoflakes demonstrated impressive pseudocapacitive performance, with a specific capacitance of 357 Fg^{-1} at 1 Ag^{-1} and cyclic stability of 84% capacitance retention and 98.5% Coulombic efficiency after 2000 cycles at 5 Ag^{-1} and V-LTO@24 showed remarkable electrochemical properties with a high specific capacitance of 442 F/g with excellent rate capability and cycle stability that surpass those of pure LTO@24.

Keywords: $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes; hydrothermal synthesis; microstructure; vanadium doping; electrochemical properties; supercapacitors

1. Introduction

The fast-increasing energy crisis and depletion of fossil fuel have instigated researchers for the exploration of efficient energy storage systems such as batteries and supercapacitors. Batteries have been the most utilized energy devices owing to high energy capacity, whereas the capacitors remain the suitable device even to date when substantial energy is required at high power. However, they have been encountering several bottlenecks such as short life cycles and shelf lives for the current solutions [1–6]. In recent times, supercapacitors, have been observed as fabulous consideration due to their high energy density, excellent reversibility, rapid charge-discharge capability and long cycling life. The development of flexible, light weight, environmentally friendly and efficient energy storage devices with high energy and power densities is mainly depending on the fabrication of suitable electrode material with required properties and is one of the key issues of current research [7–9].

Transition-metal oxides (TMOs) have been extensively studied as electrode materials due to their superior physicochemical properties such as multiple valences, electrical conductivity, fast ion/electron transport, good structural stability as electrodes in high efficiency lithium-ion batteries (LIBs) and supercapacitors (SCs). Though the transition-metal oxides have the advantages of avoiding the formation of Li dendrites, numerous challenges such as poor intrinsic electrical conductivity, electrode powdering resulting from significant volume alteration, voltage lag between charge –discharge and electrode decomposition are yet to be addressed [10–12]. Many transition-

metal oxides (TMOs) such as RuO_2 , MnO_2 , NiO , Co_3O_4 , MoO_3 , LiCoO_2 , LiMn_2O_4 , NiCoO_2 , MnCoO_2 , $\text{M}(\text{OH})_2$ ($\text{M}=\text{Ni}$, Fe , Co , Mn), Li_2TiO_3 , etc., have been commercially employed in LIBs and supercapacitors [13–21]. Among TMOs, lithium titanate (LTO) represents a significant member of the solid solution $\text{Li}_{3-x}\text{Ti}_{6-x}\text{O}_{12}$ ($0 \leq x \leq 1$) family. The crystal structure of the LTO belongs to the $Fd\bar{3}m$ space group, in which one part of the Li^+ is located at $8a$ Wyckoff sites, all Ti-ions, and another part of Li^+ are located at $16d$ sites with a ratio of $\text{Li}:\text{Ti} = 1:5$, and oxygen-ions occupy the $32e$ sites. In-light of these observations, it can be posited that LTO can be described as $\text{Li}_{3(8a)}[\text{LiTi}_{5(4d)}]\text{O}_{12(32e)}$. The spinel lithium titanate (LTO) is a potential anode material which can replace graphite anodes as it exhibits high full cell power density of $\sim 10 \text{ kW kg}^{-1}$, two times greater than graphite anode. It exhibits outstanding structural stability and zero strain during intercalation, ensuring outstanding safety and capacity retention. It reveals high lithiation and delithiation voltage of $\sim 1.55 \text{ V}$ with Li insertion and effectively avoids the formation of Li dendroid. In addition, excellent pseudo capacitive behavior, a Faradaic process involving surface/near-surface redox reactions, has been detected in some modified LTO to surmount the limit of theoretical capacity by boosted lithium storage providing high power and energy densities in wide temperature range. However, the poor electronic conductivity due to lack of electrons in $3d$ orbital of Ti and low Li diffusion co-efficient impeding the electrochemical performance of LTO for practical use in LIBs and SCs [22–25]. The pseudocapacitive response of LTO can be markedly enhanced by employing synergistic effects of multiple modifications by creating additional active sites. Intensive investigations have been made over the past one decade to improve reversible specific capacity and superior rate capability by adopting several strategies such as morphological engineering by optimizing the size and shape of nanoparticles, doping with a suitable metallic or non-metallic ions, formation of nano composite with carbonaceous materials (CNTs/rGO), heterogeneous phase control, etc. Several researchers synthesized LTO in various compositions and nano structural designs utilizing various fabrication techniques, to improve the electrochemical performance for utilization in high efficiency energy storage devices. Recently, to enhance the electrical conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, many researchers reported the effect on the crystal and electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, by doping various transition metal cation into Li or Ti site such (Cr^{3+} , V^{5+} , Ta^{5+} , Co^{3+} , Cu^{2+} , Ga^{3+} , Sc^{3+} , Fe^{3+} , Mg^{2+} , Mn^{4+} , and Nb^{5+}) in Li or Ti sites [26,27].

Among the potential dopants, vanadium is distinguished as a noteworthy candidate owing to its superior electrical conductivity and redox properties. Vanadium oxides have been extensively researched as electrochemical energy storage materials for supercapacitors and lithium-ion batteries due to their capacity for redox intercalation, attributed to the diverse oxidation states of vanadium (+2, +3, +4, and +5) and V is an exceptionally suitable dopant for LTO, as it maintains the integrity of its phase and lattice parameters. This result can be attributed to the compatibility between ionic radii of Ti^{4+} and V^{5+} [8]. Multiple reports discussed the electrochemical performance of LTO and vanadium-doped LTO in the context of Li-ion batteries and hybrid supercapacitors [28,29]. A detailed review on advanced pseudocapacitive lithium titanate towards next-generation energy storage devices was reported by Ge et al. [23]. Several researchers reported the synthesis of LTO in typical surface morphologies including nanoparticles, nanowires and nanosheets and demonstrated notable pseudocapacitive contributions. Batsukh et al. [30] synthesized LTO materials via solid-state method. The ideal stoichiometric ratio for doping lithium titanate was determined to be $x = 0.075$, as it produced the maximum specific capacitance of 3.59 F/g and a reduced band gap value of 3.13 eV . Consequently, this study offers additional support for the utilization of LTO electrodes in aqueous capacitors and electrical applications. Tian et al. [31] synthesized LTO consisting of ultrafine nanowires by ion exchange process in liquid phase environment and demonstrated specific capacity of $\sim 178 \text{ mAh/g}$ at 200 mA/g even after 2500 cycles. Xing et al. [26] synthesized three-dimensional flower shaped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -graphene hybrid micro/nanostructures and pine needles derived carbon nano-pores by effective hydrothermal process and demonstrated specific capacitance of 706 F/g and 314 F/g at 1 A/g , respectively, with good cycle retention of 90% after 2000 cycles. Lee et al. [32] reported a high specific capacitance of 63 F/g for the fabricated asymmetric hybrid supercapacitors composed of granule $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as an anode and activated carbon as cathode.

The current research work involves, the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes by the hydrothermal technique at various reaction times and optimized with respect to the microstructural properties. The synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes at a reaction period of 24 h, demonstrated exceptional pseudocapacitive performance, achieving a specific capacitance of 357 F/g at a current density of 1 A/g. For further enhancement of electrical conductivity and hence the specific capacitance, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is doped with vanadium and reported a high specific capacitance of 442 F/g at 1 A/g current density with excellent rate capability and cycle stability.

2. Materials and Methods

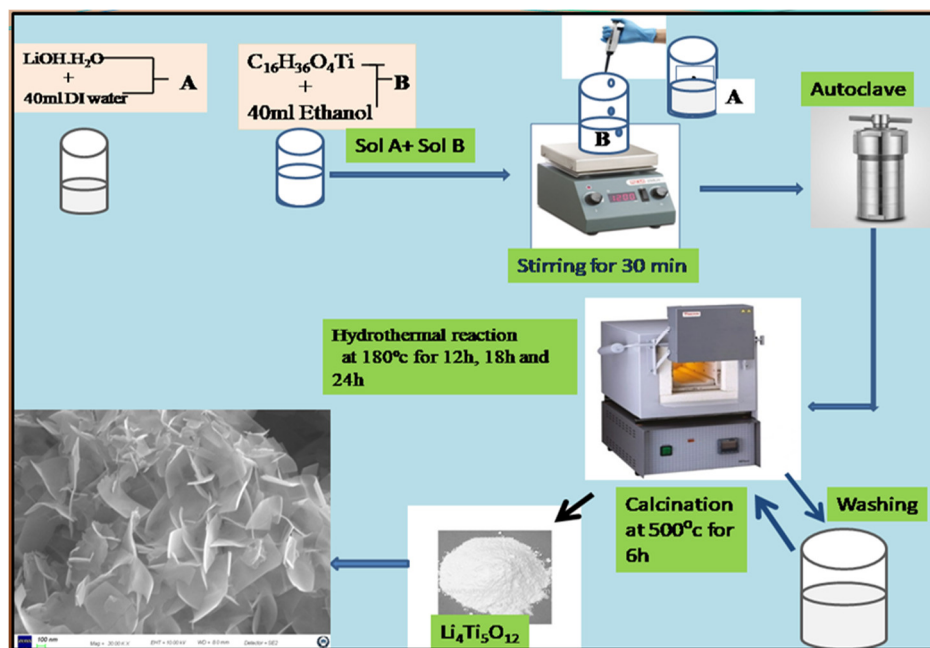
The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

2.1. Materials

The chemicals used during synthesis were lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$ USA), titanium(IV) butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, $\geq 97\%$ Sigma-Aldrich, USA), ammonium metavanadate (NH_4VO_3 , 99%, SDFCL), ethanol ($\text{C}_2\text{H}_5\text{O}$), and DI water. No additional purification procedures were implemented; all compounds were utilized entirely as received.

2.2. Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanomaterial

Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were synthesized utilizing the hydrothermal technique (see Scheme 1). In a typical synthesis method, 4.2 mM of lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) is dissolved in 40 mL of deionized water to make solution 1, while 5 mM of titanium(IV) butoxide is dissolved in 40 mL of ethanol to create solution 2. Both solutions are stirred continuously for 30 minutes separately. Subsequently, solution 1 is added dropwise to solution 2 while under magnetic stirring. Upon completion of stirring, the homogenous solution is transferred into a 100 mL autoclave (Teflon-lined). The temperature of the autoclave was maintained at 180 °C. The samples were prepared at various reaction durations ($\tau = 12, 18, \text{ and } 24 \text{ h}$). The acquired material was purified and washed four times with distilled water and ethanol to ensure the solution free of impurities. The resultant precipitate was dried at 80 °C for 5 h. Further the final products were calcinated at 500 °C for 6 h, with a heating rate of 3 °C per minute, to yield $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanopowders (hereinafter referred to as $\text{LTO}@\tau$).



Scheme 1. Schematic representation of the LTO synthesis via the hydrothermal method.

2.3. Preparation of V-LTO@24 ($\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$)

A similar methodology has been employed for the synthesis of vanadium-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles. This involved the addition of stoichiometric amounts of ammonium meta vanadate at a concentration of 0.02% M, while maintaining a hydrothermal reaction time of 24 h. The products were subjected to calcination in a muffle furnace at 500 °C for a duration of 6 h to obtain the final products, designated as V-LTO@24.

2.4. Material Characterizations

The structural properties of the synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were examined using an X-ray diffractometer (XRD, MiniFlex II, Rigaku, Tokyo, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). The microstructure and surface morphology of all synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder was analyzed using a field emission scanning electron microscope (FESEM, Merlin Compact, Carl Zeiss, Jena, Germany) and a high-resolution transmission electron microscope (TEM, Tecnai G2 F30, FEI Company, Oregon, USA). The elemental composition and valence state of the synthesized samples were analyzed using X-Ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos). The evaluation of the electrochemical performance of the synthesized materials was performed via cyclic voltammetry (CV), galvanostatic charge and discharge (GCD), and electrochemical impedance spectroscopy (EIS) utilizing the commercial electrochemical workstation CHI 608C (Instrument Inc., USA). EIS data were collected over a frequency range from 1 Hz to 100 kHz at an amplitude of 5 mV.

2.5. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Electrode Preparation

Electrochemical evaluations were conducted at room temperature using a three-electrode setup, with silver as the reference electrode and platinum as the counter electrode. For the preparation of the working electrode. Ni foam was utilized, which underwent cleaning with 6 mol/L HCl, deionized water, and 100% ethanol for 20 min each under ultrasonication to eliminate the surface layer of the Ni foam, followed by drying at 80 °C for 10 h. Subsequently, the composite comprising active material LTO@24 (80%), activated carbon black (10%), and PVDF binder (10%) was suspended in 0.5 mL of NMP solution. Activated material slurry is applied to cleaned Ni foam across an area of $0.7 \times 1 \text{ cm}^2$ using a drop-casting technique and then dried at 80 °C for 8 h. A 1 mol/L KOH solution served as the electrolyte for all experiments.

3. Results and Discussion

3.1. Studies of Pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Nanoflakes

3.1.1. XRD Analysis

The X-ray powder diffraction analysis was employed to confirm the crystalline structure and phase purity of the hydrothermally synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes. Figure 1 illustrates the XRD spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanopowders synthesized at various reaction time periods. The XRD spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized for 12 and 18 h displayed an additional minor anatase (A) and rutile (R) phase of TiO_2 at $2\theta = 25.30^\circ$ (JCPDS card 21-1272) and $2\theta = 27.47^\circ$ (JCPDS card 12-1276), respectively, alongside $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. This phenomenon may be attributed to inadequate reaction times, leading to incomplete phase transformation and the presence of residual TiO_2 [33,34]. By extending the reaction time to 24 h, the XRD reflections associated with the TiO_2 phases are no longer present, while peaks corresponding to the cubic spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase emerged. The diffraction peaks observed at 2θ values of 18.30° , 35.48° , 43.18° , 47.38° , 57.25° , 62.77° , and 66.13° correspond to the (111), (311), (400), (331), (333), (440), and (531) planes of cubic spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS card 49-0207) with the $Fd\bar{3}m$ space group [35–37]. The results indicated that the product progressively converted to the pure cubic spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by the extension of reaction time to 24 h.

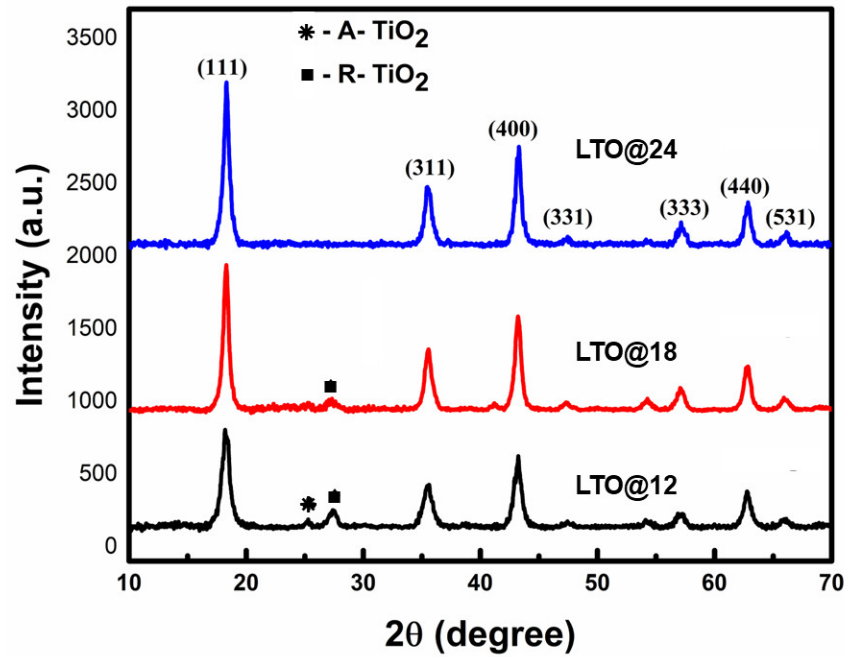


Figure 1. XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes synthesized hydrothermally at various time periods. Marks ■ and * indicate the presence of the A- TiO_2 and R- TiO_2 phases, respectively.

The Debye-Scherrer formula (Equation 1) was used to determine the crystallite size (L) of the as-produced samples using all XRD reflections:

$$L = \frac{k\lambda}{\beta \cos \theta'} \quad (1)$$

where k is equal to 0.9, λ is the wavelength of X-ray radiation, β is the full width at half-maximum (FWHM) and θ is the Bragg angle. Additionally, dislocation density (δ), microstrain (ϵ), and unit volume (V) values were calculated (see Table 1) based on the following relations [35,38]:

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

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

$$V = a^3, \tag{4}$$

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}, \tag{5}$$

The results in Table 1 indicate that the size of the crystallites increases as the hydrothermal reaction time increases from 12 to 24 h. The unit cell volume of LTO synthesized at 24 h and the estimated lattice parameter value *a* deduced from Equations (4) and (5) are in good agreement with the reported value [39–41], indicating the formation of phase pure Li₄Ti₅O₁₂. Nanoparticles of smaller crystallites have a higher surface area-to-volume ratio, which is important for strengthening the electrode/electrolyte interface, facilitating quicker ion diffusion, and increasing the material's charge storage capacity.

Table 1. The structural parameters of LTO samples synthesized at various conditions.

Sample	Crystallite size (nm)	Dislocation density(δ)	Microstrain (rd)	Lattice parameter (Å)	Unit volume (Å ³)
LTO@12	11	8.27652*10 ¹⁵	0.009933	8.4117(0)	595.18
LTO@18	12	6.98751*10 ¹⁵	0.008899	8.4018(2)	593.08
LTO@24	13	6.31196*10 ¹⁵	0.00827	8.3671(8)	585.76
V-LTO@24	11.8	7.7152*10 ¹⁵	0.0088	8.3401(2)	580.11

3.1.2. Surface Morphology Analysis

The morphology of the material plays a crucial role and an essential aspect that is intricately linked to the specific surface area, diffusion pathways, surface-to-volume ratios, and consequently, the performance of supercapacitors. The surface microstructure of hydrothermal -synthesized Li₄Ti₅O₁₂ nanoparticles is characterized using FE-SEM. Figure 2 presents the SEM micrographs of Li₄Ti₅O₁₂ nanoparticles at various magnifications, prepared through the hydrothermal method at different reaction times. The influence of reaction time on surface morphology is distinctly evident in the SEM micrograph. Figures 2(a,b) show a Li₄Ti₅O₁₂ sample obtained by hydrothermal reaction at 12 h. The low magnification SEM images demonstrate the formation of interconnected nanoflakes forming three-dimensional flower like structures. In high magnification SEM images, the assembly of nanoparticles with nanoflake like structures having a rough surface, non-uniform size, and thinner nanoflakes with uneven edges, may be due to the short hydrothermal reaction times. The surface morphology was seen to alter when reaction time varied from 12 to 18 h. As growth improves, nanoflakes develop a smooth surface, uniform size, and well-defined edges, as seen in Figure 2(c,d). Furthermore, prolonging the reaction period to 24 h resulted in the formation of well-defined, smooth surface with assembly of relatively uniform length of the nanoflakes, which were about 60 nm long and 20 nm wide as shown in Figure 3(e,f). Because of the prolonged reaction time, the flakes became firmly packed together and eventually formed a micro-network. These results indicate that the reaction time has a significant impact on the surface morphology of nanostructures. The dimensional nanoflakes have porous nature and good surface area and this structure should significantly minimize the resistance associated with electrolyte penetration and diffusion, while facilitating rapid ion and electron transfer. Additionally, it offers an ample effective area for interactions between electrolyte ions and active materials, enhancing Faradaic reactions during electrochemical process [42–45].

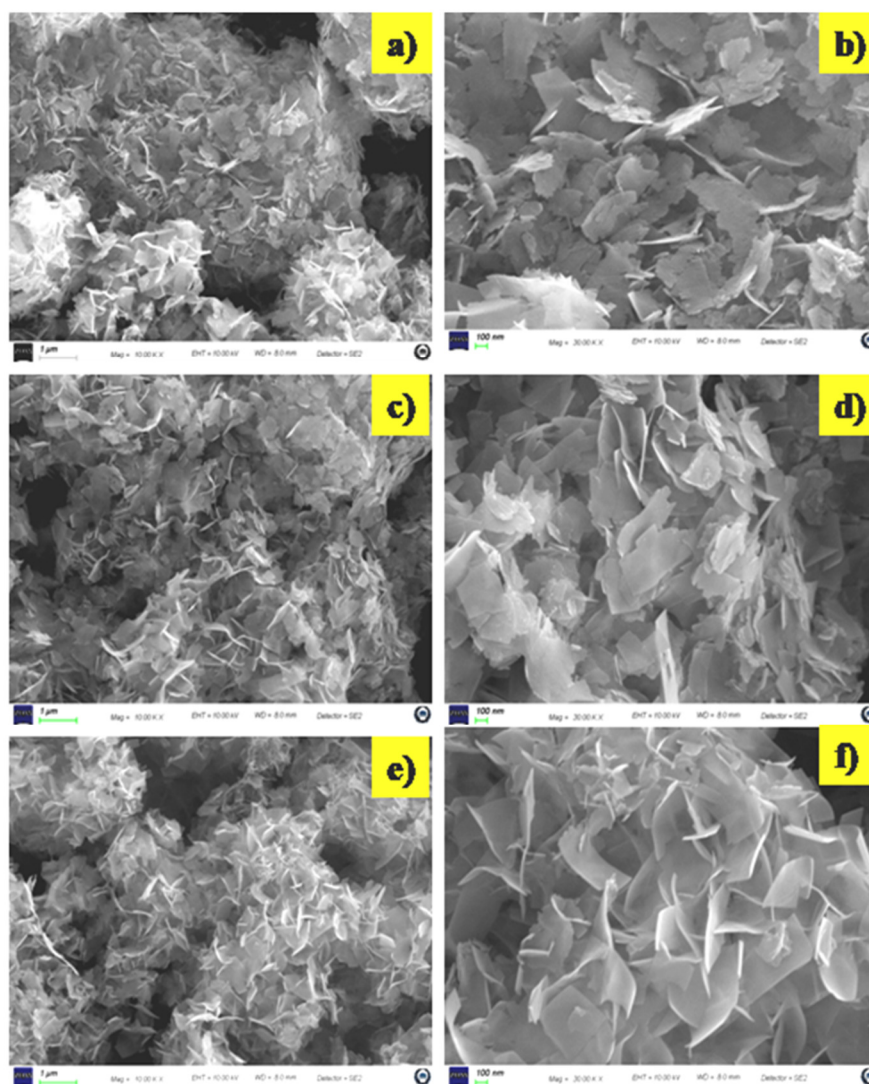


Figure 2. FESEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized at different reaction times: (a,b) 12 h, (c,d) 18 h, and (e,f), 24 h.

HRTEM is used as a representative to further characterize the shape and structure of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes. Figure 3 displays the typical TEM micrographs for the 24-h sample. The TEM image in Figure 3(a) demonstrates comparable structural characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes, consistent with the observations made in the SEM images. The HRTEM image presented in Figure 3(b) indicates that the interplanar distance between adjacent lattice fringes measures 0.48 nm, which aligns with the (111) interplanar spacing of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The Fourier transformation (FFT) derived from the HRTEM image of nanoflakes distinctly reveals a symmetrical pattern, as illustrated in the inset of Figure 3(b). The selected area electron diffraction (SAED) pattern is presented in Figure 3(c), which can be indexed to the diffraction planes of (111), (222), (331), and (531) of the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase, indicating the polycrystalline nature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. HRTEM pictures shown in Figures 4(b) and 4(c) confirm the phase purity of the produced $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes.

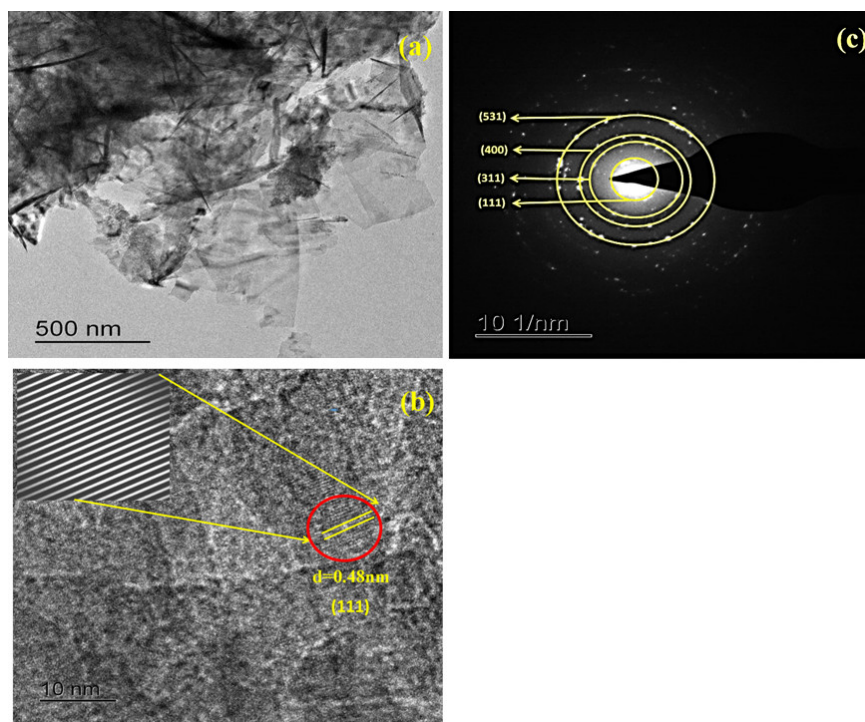


Figure 3. Microstructural features of LTO@24: (a) TEM image, (b) HRTEM image showing the lattice fringe of 0.48 nm, and (c) SAED pattern.

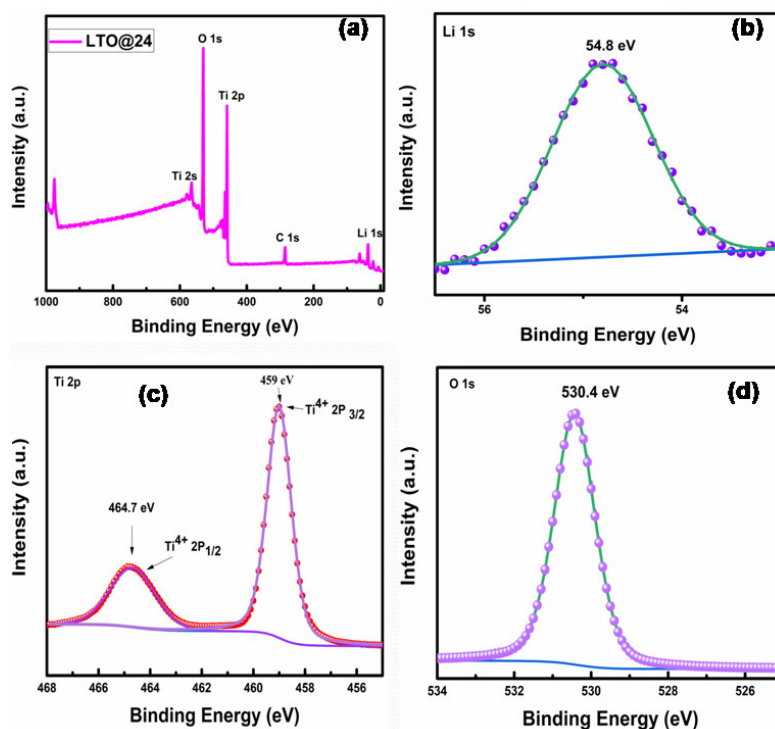


Figure 4. (a) XPS survey of LTO@24, (b, d) High resolution XPS spectra of Li 1s, Ti 2p, and O-1s.

3.1.3. XPS Analysis

The XPS studies were conducted to analyze the chemical composition and metal oxidation states of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ @24 nanoflakes as shown in Figure 4

The presence of Li, Ti, and O elements is confirmed by the XPS survey spectrum presented in Figure 4(a) The Li 1s core level XPS spectrum shown in Figure 4(b) in the low binding energy region

displays a Li 1s peak at 54.8 eV, which is attributed to the Li-O bond within the LTO spinel structure. The Ti 2p core level XPS spectrum, as illustrated in Figure 4(c) displays a distinct set of doublet peaks, with the Ti 2p_{1/2} and 2p_{3/2} lines observed at approximately 464.7 eV and 459 eV, respectively, which are indicative of the Ti⁴⁺ state. As shown in Figure 4(d) The O 1s peak is generally observed at approximately 530.4 eV, which corresponds to oxygen within the lattice, specifically in metal-oxygen bonds. The presence of core level binding energy peaks is in good agreement with the reported values and confirm the phase purity and chemical purity of the LTO spinel phase [26].

3.1.4. Electrochemical Analysis

The electrochemical properties of Li₄Ti₅O₁₂ nanoflakes synthesized at the optimized reaction time of 24 h (LTO@24) were examined through cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy (see Figure 5). The measurements are carried out by three-electrode system in 1 mol/L KOH aqueous electrolyte. Figure 5(a) shows the CV tests measured at different scan rates from 1 to 50 mV/s in the potential range of -0.3–0.6 V vs. Ag/AgCl. The CV curves of LTO@24 electrode showed the pseudocapacitive nature and observed CV curves exhibited similar shape with a couple of redox peaks and can be attributed to the reversible faradic reactions occurred on the surface and in the interlayer structure of the nanostructured LTO@24 electrode. The position of anodic and cathodic peaks is shifted as the scan rate increases, indicating outstanding high-rate performance and good electrochemical reversibility. This is beneficial for improving charge-discharge performance. Additionally, the total charge accumulated in the LTO@24 electrode as the result of the redox reaction was determined using the area under the current-voltage curve at a constant scan rate. The specific capacitance C_s of the electrode at each scan rate was calculated using the subsequent Equation (6) [46]:

$$C_s = \frac{1}{mv\Delta V} \int_{V_a}^{V_c} I(V)dV, \quad (6)$$

where v is the potential scanning rate, m denotes the mass of active material in the electrode, and $\Delta V = V_c - V_a$ represents the potential window for the discharging process. The specific capacities of the LTO@24 electrode were determined to be 123, 92, 80, 64, and 57 F/g at scan rates of 1, 5, 10, 30, and 50 mV/s, respectively. The area enclosed by the cyclic voltammetry (CV) curves was used to evaluate the capacitive performance of the electrode samples, as it is directly proportional to their specific capacitance. As the scan rate increased from 1 to 50 mV/s, the specific capacitance decreased. This is because, at higher scan rates, the time available for the charging process is reduced, resulting in incomplete charge storage and a lower apparent capacitance.

The GCD measurements were conducted under identical experimental circumstances for the LTO@24 nanoflake electrodes. The GCD measurements are conducted from -0.3 to 0.4 V vs. Ag/AgCl at various current densities ranging from 1- 5 A/g, with the findings presented in Figure 5(b). The GCD curves exhibit non-linear behavior, indicating a pseudocapacitive charge storage mechanism resulting from fast faradic redox reactions in the LTO@24 nanoflakes of the electrodes. This demonstrates that the electrodes of LTO@24 nanoflakes validate the pseudocapacitive behavior, consistent with the CV curves. The specific capacitance C_s can be determined using the GCD curves using the following Equation (7) [46,47]:

$$C_s = \frac{I\Delta t}{m\Delta V}, \quad (7)$$

where I is the discharge current, m is the mass of the active material, ΔV is the potential window, and Δt is the discharge time. According to the data shown in Figure 5, the determined specific capacities of the LTO@24 nanoflakes electrode are 357, 128, 107, 85 and 40 F/g at current densities of 1, 2, 3, 4 and 5 A/g, respectively. It is evident that specific capacitance decreases as current density escalates. The observed decrease in capacitance can be ascribed to the restricted duration for electrolyte ions to infiltrate the active material when subjected to elevated current densities. At reduced current densities, the electrolyte ions are afforded ample time to distribute uniformly throughout both the

interior and surface of the active material, leading to an enhancement in specific capacitance [48,49]. Consequently, the nanoflake-like architecture of LTO@24 not only reduces the ion diffusion distance but also enhances the available surface area for redox reactions.

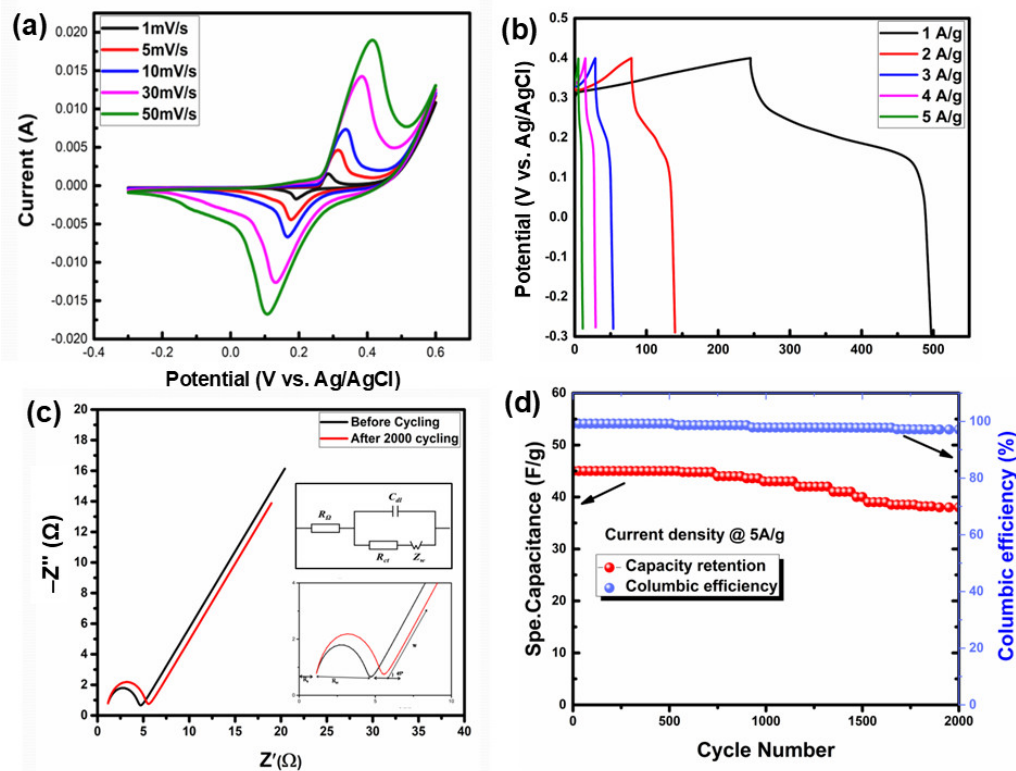


Figure 5. Electrochemical characteristics of the LTO@24 nanoflakes. (a) Cyclic voltammetry curves recorded at different scan rates. (b) Galvanostatic charge discharge curves carried out at different current densities of 1-5 A/g in the potential range from -0.3 to 0.4 V vs. Ag/AgCl. (c) Nyquist plots before and after long-term cycling. Inset shows the equivalent circuit model. (d) Cycling stability performed at a current density of 5 A/g.

In order to assess the ion diffusion, electrical conductivity, and electron transfer characteristics of the LTO@24 nanoflakes electrode, electrochemical impedance spectroscopy (EIS) measurements were conducted prior to and following 2000 cycles, across a frequency spectrum of 1Hz to 100KHz utilizing an alternating current voltage of 5 mV. Figure 5(c) illustrates the Nyquist plots of the LTO@24 electrode, characterized by the presence of a semicircular arc alongside a linear segment in the low-frequency range. It indicates the characteristics of capacitive behavior and rapid ion diffusion within the electrode. The intercept on the X-axis represents the solution resistance (R_s), which encompasses the ionic resistance in the electrolyte, the contact resistance of the current collector and active material, as well as the intrinsic resistance of the active material. The diameter of the semicircle is indicative of the charge transfer resistance (R_{ct}) at the interface between the electrode and the solution. The slope of the straight line in the low frequency region indicates the Warburg impedance (Z_w), which is linked to the diffusive resistance of OH. The diameter of the semicircle and the slope of the line were altered following 2000 cycles (inset of Figure 5(c)), which is probably a result of the repetitive mechanical stress occurring during the continuous charge-discharge process. The analogous electrical circuit is depicted in the inset of Figure 5(c). The R_s values are recorded at 0.7 and 0.8 Ω prior to and following cycling, whereas the R_{ct} values show an increase from 2.18 to 4.8 Ω. The analysis demonstrates that the distinctive structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoflakes has the potential to enhance the active sites for Faradic reactions while also reducing the transfer distance for ions and electrons. Therefore, enhanced kinetics and improved electrochemical performance of the electrode can be attained.

Figure 5(d) illustrates the long-cycle performance and Coulombic efficiency of the LTO@24. The cyclic stability holds significant importance for supercapacitor applications; therefore, an extensive examination of long-term cycling performance was conducted through charge-discharge cycling at a current density of 5 A/g. Additionally, Coulombic efficiency (η) serves as a crucial parameter for assessing the viability of the redox process, with the value of η derived from the subsequent Equation (8) [50]:

$$\eta = \frac{t_d}{t_c} \times 100, \quad (8)$$

In this context, t_d and t_c denote the times associated with discharge and charge, respectively. Throughout the 2000 charge-discharge cycling process, the η values remain remarkably stable at approximately 98.5% for the entire duration, signifying the exceptional electrochemical reversibility of the Faraday reactions. These results demonstrate that LTO@24 nanoflakes represent a promising electrode material, exhibiting improved physicochemical properties, and can be effectively utilized in electrochemical energy storage devices.

3.2. Vanadium-Doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (V-LTO@24)

The vanadium doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (V-LTO@24) nanopowder was prepared under similar conditions as mentioned in Section 2.3 at low concentration (0.02 mol.%) and studied the microstrural and electrochemical properties.

3.2.1. Structural Studies

Figure 6(a) presents the X-ray diffraction patterns of V-LTO@24 ($\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$; $x=0.02$ mol.%) compared with pure LTO@24. The diffraction peaks of pure and V-LTO@24 powders are attributed to the cubic spinel structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS No. 49-0207) with the $Fd\bar{3}m$ space group. No undesired impurities or new phases were observed in samples with a lower concentration of vanadium dopant ($x = 0.02$), thereby affirming the successful incorporation of the vanadium ion into the lattice of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without the emergence of any additional phases. Moreover, upon magnifying the peak location of the (111) plane, as seen in Figure 6(b) the diffraction peak of V-LTO@24 nanoflakes exhibits a minor shift towards a higher angle, suggesting that the doping of V has infiltrated the lattice structure of LTO nanoflakes. The XRD of the V-LTO doped sample showed a slight shift in the diffraction peak towards larger θ values than that observed for the pure LTO sample. This peak shift is associated with the atomic radius disparity between Ti^{4+} and V^{5+} elements. In the coordination $CN = VI$, the atomic radius of V^{5+} (0.54 Å) is smaller than that of Ti^{4+} (0.605 Å) [8], leading to a diffraction shift towards a larger angle. These results indicate that the V^{5+} is successfully substituted Ti^{4+} in the spinel lattice structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

The influence of doping on the structural modifications of LTO@24 and V-LTO@24, specifically focusing on lattice parameters, unit cell volume, and average crystallite size, using Equations (4), (5), and (6). The calculated structural parameters are listed in Table 1. The results show that the lattice parameters of V-LTO@24 are marginally smaller than those of LTO@24. Specifically, the lattice parameter of V-LTO@24 ($a = 8.340$ Å) is lower compared to that of LTO@24. This reduction suggests that V doping has induced a lattice shrinkage in the material. Such a phenomenon can be attributed to the substitution of Ti^{4+} ions ($r_i = 0.605$ Å) by smaller V^{5+} ions ($r_i = 0.54$ Å) within the spinel lattice structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The relatively close ionic radii facilitate the incorporation of V^{5+} into the Ti^{4+} sites with minimal distortion to the overall crystal framework. The replacement of Ti^{4+} with the smaller V^{5+} ions leads to a slight contraction of the lattice, consistent with the observed decrease in lattice parameters and unit cell volume. Furthermore, the effective incorporation of V^{5+} into the LTO spinel structure indicates successful doping, which is known to significantly influence the electrical conductivity of the host material. Such structural and electrical modifications can directly impact the electrochemical properties, potentially enhancing the material's performance in supercapacitor applications, as supported by previous literature [28,29].

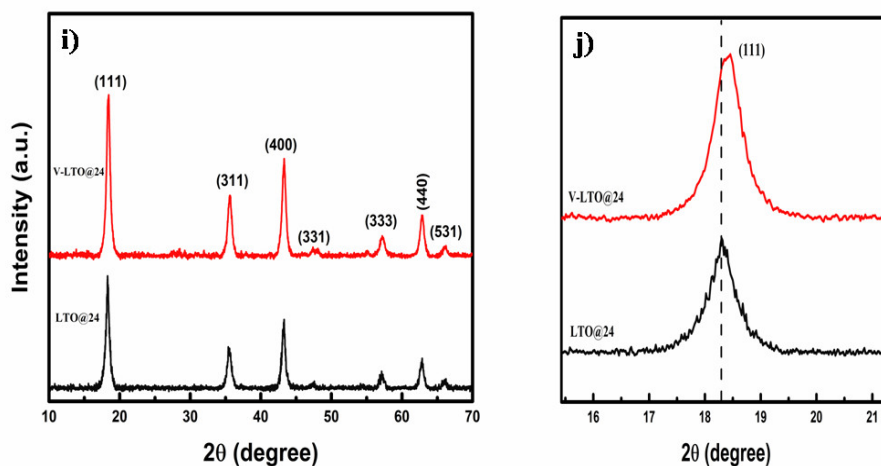


Figure 6. (a) XRD pattern of LTO@24 and V-LTO@24 and (b) expanded XRD spectrum in the vicinity of the (111) reflection.

3.2.2. Surface Morphology

The surface morphology of V-LTO@24 is shown in Figure 7. The nanoflakes evidently aggregate to create a three-dimensional nanoflower-like structure. Nonetheless, upon vanadium introduction into LTO@24, an effect of doping was noted on the surface morphology. The addition of vanadium resulted in a tighter packing of nanoflakes and the emergence of micro-network-like structures from the recrystallisation of initially formed nanoflakes. The vertically orientated arrays cross and interpenetrate, creating porous network-like heterostructures. This would offer significantly elevated active surface sites, together with appropriate routes and reduced diffusion lengths for ionic transport, which would be very advantageous for enhancing the electrochemical characteristics of the samples.

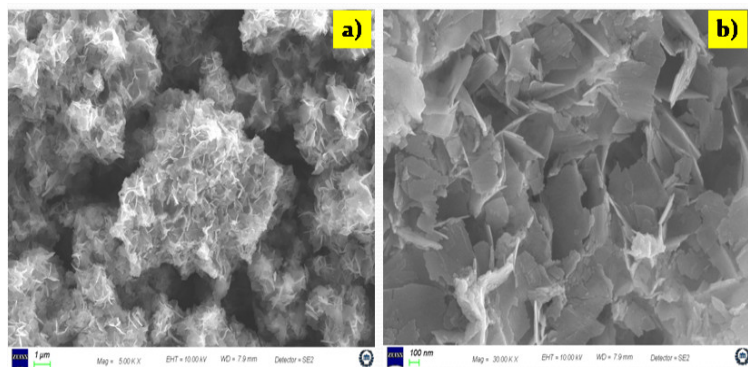


Figure 7. FESEM images for V-LTO@24 nanoflakes at different magnifications: (a) 1 μm scale, (b) 100 nm scale.

3.2.3. Electrochemical Analysis of V-LTO@24

Figure 8 presents the comprehensive electrochemical performance of V-LTO@24 electrodes examined via typical three-electrode experiments using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy techniques, with a 1 mol/L KOH solution as the electrolyte. Figure 8(a) illustrates the CV curves of V-LTO@24 at scan rates of 1, 5, 10, 30, and 50 mV/s within a potential range of -0.3 to 0.6 V vs. Ag/AgCl. All the cyclic voltammetry curves display a pair of redox peaks with a characteristic pseudocapacitive behavior and an exceptional rate capacity. With an increase in scan rate, the region beneath the redox peaks expands, indicating an improvement in current responsiveness. Furthermore, as a result of the polarization of the electroactive material, the anodic peaks exhibit a substantial shift towards more positive potentials,

whilst the cathodic peaks shift towards more negative potentials with an increased scan rate. This transition is due to the lower resistance and fast ion and electron movement within the electrode. The pronounced and distinct redox peaks are intricately linked to the chemical composition and form of the electrode material, which promote reversible faradaic redox processes. The specific capacitance (SC) of V-LTO@24 nanostructures was assessed at various scan rates in the range 1-50 mV/s using Equation (2) to quantitatively evaluate their electrochemical performance. The C_s values were found to be 413, 188, 135, 83, and 66 F/g at scan rates of 1, 5, 10, 30, and 50 mV/s, respectively. As the scan rate increased, a gradual decrease in specific capacitance was observed, which can be attributed to limited ion diffusion and reduced charge storage efficiency at higher scan rates.

The capacitive performance of the synthesized V-LTO@24 electrodes was thoroughly assessed using galvanostatic charge-discharge (GCD) measurements. Figure 8(b) represents the GCD curves recorded at current densities of 1, 2, 3, 4, and 5 A g⁻¹ within a potential window ranging from -0.3 to -0.4 V vs. Ag/AgCl. An in-depth examination of these curves demonstrated the outstanding capacitive properties of the V-LTO@24 electrodes. The specific capacitances were systematically calculated using Equation (7) and found to be 442, 285, 171, 142, and 80 F g⁻¹ at current densities of 1, 2, 3, 4, and 5 A g⁻¹, respectively. The results demonstrate the outstanding rate capability and strong electrochemical performance of the V-LTO@24 electrodes across a broad spectrum of current densities. Additionally, all GCD curves demonstrate a clear potential plateau and remarkable symmetry, affirming the high Coulombic efficiency and exceptional reversibility of the faradaic redox reactions involved.

To further investigate the electrical properties of the V-LTO@24 electrode, EIS measurements were carried out over a frequency range from 1 Hz to 100 kHz at an amplitude of 5 mV. This analysis provides critical insights into the electrode's ability to efficiently facilitate charge transfer and maintain stable performance across different frequencies. Figure 8(c) shows the Nyquist plot with the equivalent circuit of the sample for the 1st and 2000th cycle. After 2000 cycles, the solution resistance R_s (i.e., the intersection made on the horizontal axis) increased from 0.38 to 0.5 Ω , and charge transfer resistance R_{ct} (i.e., the diameter of the semicircle in the high- to medium-frequency region) increased from 0.6 to 0.9 Ω . The specific capacitance decreases with the number of cycles, as the solution and charge transfer resistance increase after 2000 cycles.

The cycle performance of the V-LTO@24 electrode was evaluated using GCD profiles at a current density of 5 A/g over 2000 cycles (Figure 8(d)). The results revealed that 90% of the initial capacitance was retained after 2000 cycles at a current density of 5 A/g, with a remarkable Coulombic efficiency of 99.8%. This indicates the excellent cyclic stability of the V-LTO@24 electrode. The superior performance of the V-LTO@24 electrode, compared to pure LTO nanoflakes, can be attributed to the aggregation of vanadium-doped LTO into a micro-network structure. This unique structure not only improves the overall conductivity but also enhances the mechanical stability of the electrode during long-term cycling. The vanadium doping enhances the electrochemical reactivity, facilitates better ion diffusion, and minimizes structural degradation, which ultimately leads to better cycle stability and performance compared to pure LTO nanoflakes.

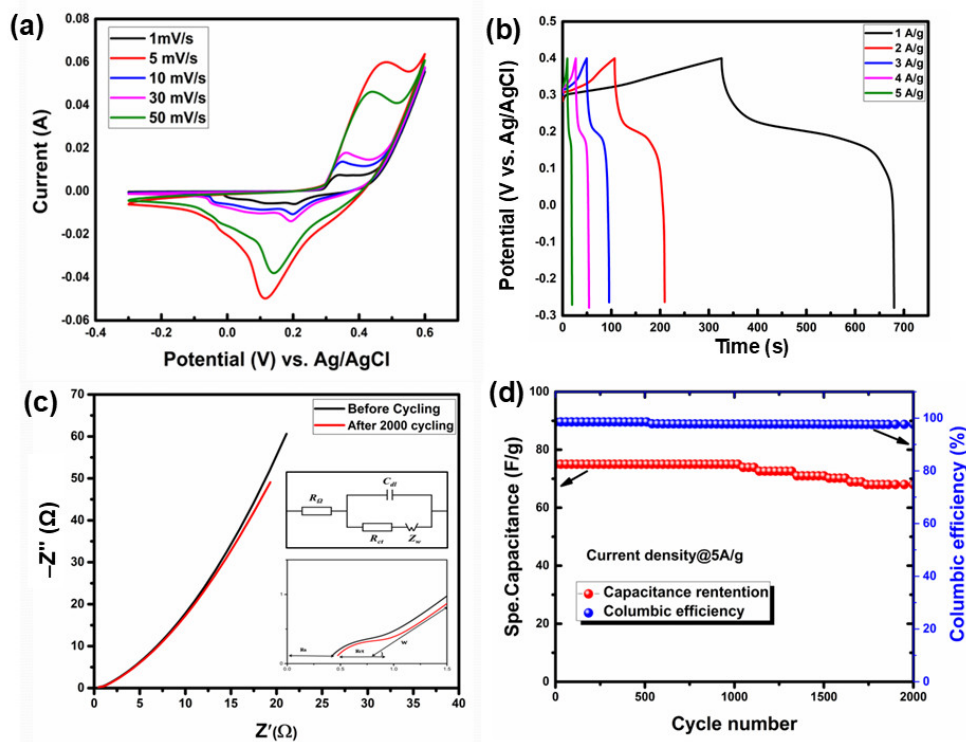


Figure 8. Electrochemical characteristics of the V-LTO@24 nanoflake electrode. (a) CV curves recorded at different scan rates from 1 to 50 mV/s. (b) GCD profiles at different current densities. (c) Nyquist plots of before (black curve) and after (red curve) long-term cycling. (d) Cycling stability of the specific capacitance and Coulombic efficiency carried out over 2000 cycles at current density of 5 A/g.

3.3. Charge Storage Mechanism in LTO-Based Electrodes

Figure 9 presents the specific capacitance of the LTO@24 and V-LTO@24 electrodes collected at different scanning rates. It is viewed that the specific capacitance C_s decreases as the scanning rate increases in the CV experiments. The decay in the specific capacitance is assigned to the presence of inner active sites that cannot completely sustain redox transitions at higher scan rates [51].

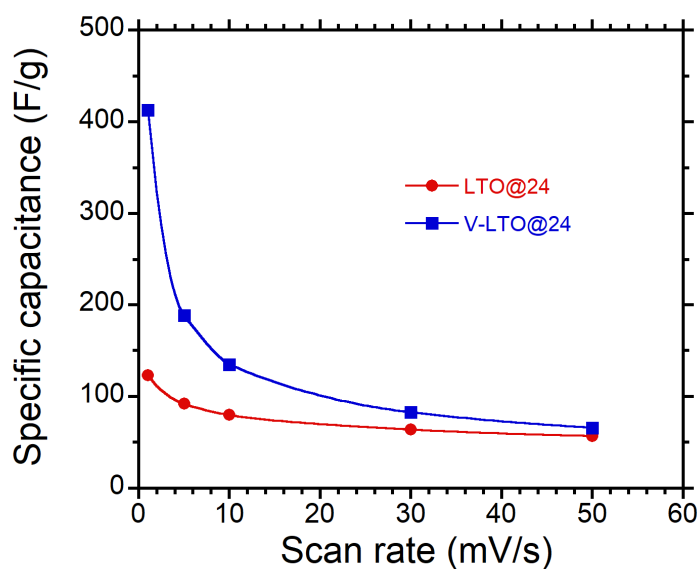


Figure 9. Specific capacitance (C_s) calculated from the CV measurements as a function of scan rate.

The reaction kinetics and charge storage mechanism in both hydrothermally prepared LTO@24 and V-LTO@24 electrodes was critically analyzed from cyclic voltammetry measurements data. The total contribution to capacitance arises from processes that are both diffusion-controlled and capacitive-controlled. Moreover, the kinetic reversibility of the electrode materials is clarified by the evident linear correlation between the peak current (i_p) and the scan rate (v) in the CV curves, adhering to a power-law relationship, as described in Equations (9 and 10) [52]:

$$i_p = av^b, \quad (9)$$

$$\log(i_p) = \log(a) + b \log(v), \quad (10)$$

where the modifiable parameters are 'a' and 'b'. The slope b of the straight line from the $\log(i_p)$ and $\log(v)$ of the plot indicates the charge storage kinetics of the ions. While the value of b equal to 1.0 suggests the capacitive process as a dominant process, the value of b equal to 0.5 suggests the diffusion control process as a dominating process. The determination of " b " values for the anodic peaks of the LTO@24 and V-LTO@24 electrodes are found to be 0.53 and 0.56, respectively (Figure 10(a,c)), indicating that the charge storage process is primarily governed by a diffusion-controlled battery-type behavior. Additionally, at various scanning speeds, the rate at which the diffusion process and surface capacitive-controlled reaction contributed to the capacitance was examined. The relative contributions of the above two processes on the overall charge storage performance are examined via Cottrell's equation [53]:

$$i_p(v) = k_1v + k_2v^{1/2}, \quad (11)$$

where k_1 and k_2 are constants for specific sweep rates, $i_p(v)$ denotes the peak current at a given potential value, and k_1v and $k_2v^{1/2}$ are terms which stand for the capacitance-controlled and diffusion-controlled processes, respectively. The above Equation (11) can be expressed as:

$$i_p(v) v^{-1/2} = k_1 v^{1/2} + k_2. \quad (12)$$

By only graphing the correlation between i_p and v , we may ascertain the slope k_1 . By determining the k_1 value at varying voltages across different scan rates [54–56], the relative contributions of the battery-type (diffusion-controlled) and capacitive-type (surface-controlled) behaviors at various scan rates of 1, 5, 10, 30, and 50 mV/s for LTO@24 and V-LTO@24 electrodes are illustrated in Figure 10(b,d). The LTO@24 and V-LTO@24 electrodes clearly demonstrate a more significant level of diffusion-controlled charge storage at all scan rates. Additionally, it has been noted that the ratio of capacitive participation across all electrodes progressively rises from lower to higher scan speeds, which can be explained by the restricted time for ions to diffuse into the internal structure of the electroactive materials.

The detailed in-depth studies of electrochemical behavior and fundamental mechanisms of the V-LTO@24 electrode uncovered several critical factors that showed enhance supercapacitive performance, especially regarding ion transport, electron transfer processes, and microstructure. The distinctive morphology of the V-LTO@24 structure, featuring aggregated nanoflakes in a micro-network-like arrangement, is characterized by a large surface area that enhances ion transport efficiency. This configuration facilitates greater ion adsorption and desorption throughout electrochemical reactions and hence increased charge (or energy) storage within the electrode thereby improving the specific capacitance. Furthermore, the specific capacitance and cycling stability of the LTO@24 and V-LTO@24 materials were compared with those of previously reported LTO-based electrodes, as presented in Table 2. The results demonstrate its superior electrochemical performance in a three-electrode system compared to the earlier LTO-based electrodes.

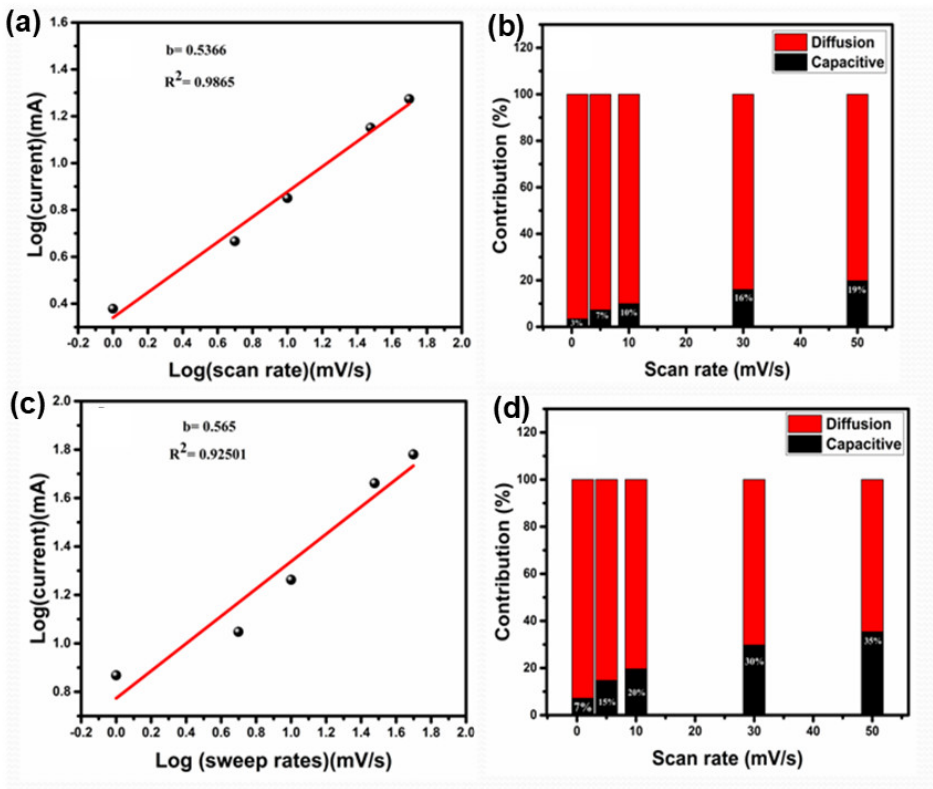


Figure 10. (a,b) Plots of $\log(i_p)$ vs. $\log(v)$ and relative contributions of the capacitive and diffusion-controlled charge storage processes of LTO@24 electrode at different scan rates. (c,d) Plots of $\log(i_p)$ vs. $\log(v)$ and relative contributions of the capacitive and diffusion-controlled charge storage processes of V-LTO@24 electrode at different scan rates.

Table 2. Comparison of the electrochemical performance of hydrothermally prepared LTO@24 and V-LTO@24 electrodes with other LTO-based electrodes recently reported in the literature.

Sample	Capacitance	Retention over cycling	Ref.
V-doped LTO	179 mAh/g @ 1C	95% (300)	[29]
Granule-LTO powders	63 F/g @ 0.5 A/g	92.8% (7000) @ 3 A/g	[32]
SSR synthesized nano-LTO	265 F/g @ 0.5 A/g	81% (5000) @ 0.5 A/g	[35]
R-TiO ₂ decorated LTO	143 mAh/g @30C	92.3% (3000)	[57]
3D chestnut shell-like LTO	653 F/g @ 1 A/g	88.5 % (4000)	[36]
LTO	83 F/g @ 2C	84% (9000) @0.98 A/g	[58]
C-modified LTO	125 F/g @ 0.55 mA/cm ²	95% (400) @ 0.4 mA/cm ²	[59]
LTO nanowire	174 mAh/g @ 2 A/g	85% (3000) @ 2 A/g	[60]
LTO-TiO ₂ nanoparticles	357 F/g @ 1 A/g	98.5% (2000) @ 5 A/g	this work
Hydrothermal LTO@24	442 F/g @ 1 A/g	99.8% (2000) @ 5 A/g	this work
Hydrothermal V-LTO@24			

4. Conclusion

In summary, Li₄Ti₅O₁₂ nanoflakes were synthesized using the hydrothermal method with varying reaction durations. The XRD spectra validate the pure phase of Li₄Ti₅O₁₂ nanocomposite

when synthesized at 24-h hydrothermal reaction time. The results from SEM and TEM indicate that the LTO@24 exhibits a morphology characterized by nanoflakes with a uniform length of approximately 60 nm, a width of ~20 nm and a relatively smooth surface. The distinct nanostructures offer an extensive surface area and minimized diffusion length, making them exceptional candidates for energy storage and conversion systems. The electrochemical investigations were conducted on the LTO@24 nanoflakes electrode using CV, GCD, and EIS experiments using a 1 mol/L KOH aqueous solution. The CV curves with marked oxidation and reduction peaks reveal the pseudocapacitive nature of the LTO electrode and demonstrate an impressive specific capacitance of 357 F/g at the current density of 1 A/g, with 84% cycle stability and 98.5% Coulombic efficiency. Moreover, the vanadium-doped LTO@24 nanoflakes synthesized under similar conditions demonstrate an excellent specific capacitance of 442 F/g at 1 A/g current density, along with 90% cycle stability and a Coulombic efficiency of 99.8%. The LTO@24 and V-LTO@24 electrodes clearly show a more significant level of diffusion-controlled charge storage at all scan rates with significant capacitance and are found to be suitable electrodes for high performance supercapacitors.

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