



Review article

Hybrid anode materials for rechargeable batteries – A review of Sn/TiO₂ based nanocomposites

Mahmood Jamil ^a, Shanghai Wei ^{a,b,*}, Mark Philip Taylor ^{a,b}, John J.J. Chen ^a, John Vedamuthu Kennedy ^{c,d}

^a Department of Chemical and Materials Engineering, The University of Auckland, Auckland 1142, New Zealand

^b NZ Product Accelerator, Faculty of Engineering, The University of Auckland, Auckland 1142, New Zealand

^c National Isotope Centre, GNS Science, Lower Hutt 5011, New Zealand

^d The MacDiarmid Institute for Advanced Materials and Nanotechnology, GNS Science, Lower Hutt 5011, New Zealand

ARTICLE INFO

Article history:

Received 16 February 2021

Received in revised form 4 April 2021

Accepted 3 May 2021

Available online xxxx

Keywords:

Li-ion batteries

TiO₂

Hybrid nanostructure

Synthesis methods

Electrochemical performance

ABSTRACT

Lithium-ion batteries (LIBs) have been used as energy storage devices for appliances of a wide range of sizes, for example, mobile phones, laptops, and electric vehicles. However, current commercial electrode materials in LIBs are facing severe challenges in energy density, safety, price, and recyclability, and this energy storage technology needs to be further developed for high power application in future. To address this challenge, nanostructured materials which possess large surface-to-volume ratios have been intensively studied as potential electrode materials to improve the battery performance. Among them, Tin (Sn) and nanostructured TiO₂ have shown some advantages and disadvantages as electrode materials, for example Sn has high storage capacity but suffer from severe volume expansion during lithiation/delithiation. On the other hand, nanostructured TiO₂ has small volume changes during Li ion insertion/extraction, but the poor ion mobility and electronic conductivity limited its electrochemical application. This review summarizes the recent development on Sn and TiO₂ based nanostructure materials, particularly the synthesis method, their structure and battery performance as anodes for LIBs. Then, we discuss the strategies of developing new electrode materials and highlight a hybrid approach for designing and synthesizing high-performance electrode materials. The latest developments and related electrochemical performance of anode materials demonstrate that design hybrid nanostructure material is a low-cost and scalable approach to produce high-performance electrode materials for high-energy LIBs.

© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

1. Introduction.....	2837
2. Tin (Sn)-based anodes.....	2837
3. TiO ₂ -based anodes.....	2838
4. Sn/TiO ₂ based anode materials.....	2839
4.1. Sn doped TiO ₂ nanostructure	2839
4.2. Sn/TiO ₂ core-shell nanostructure	2839
4.3. 3D porous nanostructure	2841
4.4. Other nanocomposite structures.....	2841
5. Hybrid approach.....	2842
6. Conclusion and outlook.....	2844
Declaration of competing interest.....	2846
Acknowledgements	2846
References	2846

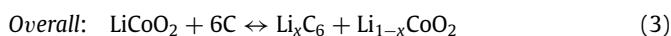
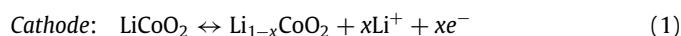
* Corresponding author at: Department of Chemical and Materials Engineering, The University of Auckland, Auckland 1142, New Zealand.

E-mail address: s.wei@auckland.ac.nz (S. Wei).

1. Introduction

Attaining a secure and sustainable energy future is one of the major challenges for the scientific and societal communities. Information Handling Services (IHS) Market stated that energy storage capacity was 6 GW globally in 2017 and it would grow exponentially (P & S Intelligence, 2019). Renewable energy sources, such as wind, solar and other carbon-neutral energy resources, are gradually replacing fossil fuels (Liu et al., 2019b). Scalable, efficient and cost-effective energy storage technologies for large scale grid connectivity and transport applications are essential (Taylor and Chen, 2015). Electrochemical energy storage systems such as rechargeable batteries, fuel cells, and supercapacitors are playing a pivotal role as supporting technologies for a sustainable and clean environment (Kulova, 2013). Among these energy storage systems, secondary rechargeable batteries, particularly Lithium-ion batteries (LIBs), have attracted significant attention and applied in various applications, including transportation, portable electronic devices, and grid energy storage. Compared to other rechargeable batteries, LIBs have high working voltage, no memory effect and various types of electrode materials and electrolytes (Kim et al., 2020). However, they are facing challenges in terms of safety, cyclability, structural stability, energy density, and high cost (Goodenough and Park, 2013).

A secondary LIB consists of working electrodes (cathode and anode), electrolyte, current collector, and separator. The first commercial secondary LIB uses LiCoO₂ (LCO) and soft-carbon as cathode and anode materials, providing an energy density of 80 Wh kg⁻¹. Later, graphite and optimized LCO have been adapted as anode and cathode materials, which improves the energy density of 190 Wh kg⁻¹ (Anon, 2019). The LCO has an layer structure in which the oxygen atoms are arranged in a cubic close-packed framework and Li⁺ and Co³⁺ ions are ordered in alternating (111) planes (Imanishi et al., 2007). The electrochemical reactions are summarized below, describing the working principle of typical LIBs (Lyu et al., 2021; Asenbauer et al., 2020).



Since the first secondary LIB commercialized in 1991, the application of rechargeable batteries has been broadened from small and medium portable electronic devices like mobile phones, digital cameras, and laptops to electric vehicles (EVs), robots and sub-grid power storage. EVs and other large portable electronic devices needs batteries with much higher energy density and much lower cost than the present LIB technology can offer. Thus, numerous studies have been conducted to improve the energy density and reduce the costs of LIBs. The improvement of energy density of LIBs can be achieved by either using high voltage cathode materials or developing high capacity anode materials. New and high-performance cathode materials such as LNO (LiNiO₂), LMO (LiMn₂O₄), LFP(LiFePO₄), NCA (LiNiCoAlO₂), and NMC (LiNiMnCoO₂) (Divakaran et al., 2020), have been developed and commercialized in LIBs. However, the anode materials in commercial LIBs are still carbonaceous, which has a limited capacity because of intercalation reaction mechanisms (Li_xC with 0 ≤ x ≤ 1/6 in graphite).

A wide range of carbon materials and non-carbon materials have been studied as high performance and high capacity anode materials in LIBs. In general, these anode materials can be categorized into three major groups based on the electrochemical reaction mechanism in rechargeable LIBs (Goriparti et al., 2014):

- a. Insertion/deinsertion materials, for instance, single wall and multi wall carbon nanotubes, graphene, graphite, porous carbon, and hard carbon-based materials etc.
- b. Conversion type anode materials, such as transition metal oxides (NiO, CuO/Cu₂O, Mn_xO_y, Fe_xO_y, TiO₂, and MoO₂ etc.), metal phosphides, sulphides, and nitrides (M_xX_y; where X = P, S, N)
- c. Alloying/dealloying materials like Si, Al, Ge, Bi, Sn and SnO₂ etc.

Table 1 summarizes the theoretical capacity, main advantages, and issues of four different anode materials in LIBs. Metal oxides, Si and Sn anode materials have much higher theoretical capacity than graphite. However, these materials also have drawbacks, such as poor cycling performance, as anode materials for LIBs. Since chemical reactions and charge transfer, in an electrochemical cell, occur at the electrode/electrolyte interface, the use of nanostructured electrode materials provides a large surface-to-volume ratio that will greatly enhance the charge/discharge reactions (Xie and Wei, 2014).

From the diffusivity term in Fick's law, we also know that diffusion time and square of the ion diffusion distance are directly related. Thus, reducing the particle size will reduce the diffusion length, improving the rate capability of electrode material (Wang et al., 2010b). Because of these advantages, much efforts have been explored in designing superior nanostructured anode materials for LIBs since the last two decades (Sun et al., 2016). In this article, we review the synthesis method, structure and battery performance of nanostructured materials based on Sn and TiO₂ as anodes in LIBs. We then summarize and highlight a hybrid approach for design and synthesis of high-performance electrode materials. We anticipate that this review article will inspire and provide references to researchers to develop high performance hybrid material for energy storage devices.

2. Tin (Sn)-based anodes

Sn, as an anode, can render very high specific capacity for electrochemical energy storage devices. For example, 994 mAh g⁻¹ for LIBs in case of Li₂₂Sn₅ (Wang et al., 2012a) and 847 mAh g⁻¹ for sodium-ion batteries (SIBs) while using Na₁₅Sn₄ (Zhu et al., 2013). Unfortunately, severe volume expansion during Li ion insertion/extraction introduces irreversible internal stresses, which causes negative consequences including the following:

- a. Pulverization of active materials
- b. Working electrode and the current collector may have weak electrical connection
- c. Inferior kinetics because of particle aggregation
- d. Unstable solid electrolyte interphase (SEI) film formation.

It is hard to eliminate the volume expansion issue of Sn during charging/discharging. However, it is possible to minimize the volume expansion by reducing Sn particle size, develop new methods of synthesis of Sn-based nanostructure materials (Chung and Liu, 2004) and introducing buffer materials with materials, such as carbon, metal oxides (Ma et al., 2019; Liu et al., 2019a), transition metal phosphides (Asanithi et al., 2012) and metals (Chen et al., 2019a).

Sn-based intermetallic compounds have also been widely studied to overcome nanosized Sn aggregation and pulverization during charging/discharging process and to enhance its battery performance. Based on electrochemical activity, a metal and its alloys can be divided into two groups: (1) electrochemically inactive and (2) electrochemically active metals. Electrochemically active metals play their part in contributing to the overall capacity of electrodes, whereas inactive metals are lacking in such

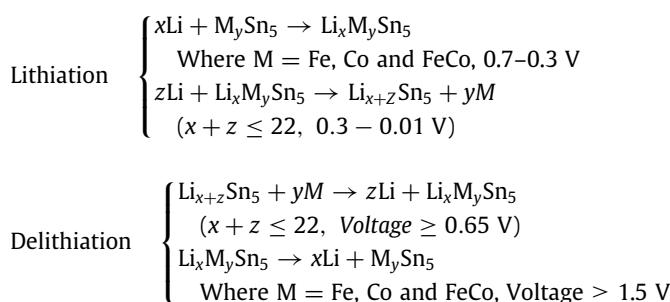
Table 1

Theoretical capacity and main issues of four most common anode materials in LIBs.

Active anode material	Theoretical capacity (mAh g ⁻¹)	Advantages	Main issues	Ref.
Graphite	372	Good safety, and low cost	Low capacity	Imanishi et al. (2007)
Metal oxides (NiO, CuO/Cu ₂ O, Mn _x O _y , Fe _x O _y , and MoO ₂)	500–1200	Low cost	Low coulombic efficiency, large potential hysteresis, and poor cycle life	Goriparti et al. (2014)
Silicon (Si)	4200	High energy density	Poor cycle life, and 400% volume change	Goriparti et al. (2014)
Tin (Sn)	993	High energy density	Poor cycle life, and 260% volume change	Goriparti et al. (2014)

characteristics. For example, Sb (He et al., 2015), Ag (Yin et al., 2003), Mn (He et al., 2018), and Ge (Cho et al., 2013) are electrochemically active materials in Li-ion batteries which can work alternatively as buffering agents for volume changes. It has been reported that Sn-based alloys, such as Co-Sn (Yang et al., 2011), Ni-Sn (Guan et al., 2014), Fe-Sn (Gao et al., 2016a), Cu-Sn (Gao et al., 2017), Ce-Sn (Sakaguchi et al., 2003), and La-Sn (Wang et al., 2009) alloys, possess the advantages of both high specific capacity and long cyclability as anodes in LIBs (Ivanova, 2017). Sn-Bi and Sn-Sb-Bi alloys (Trifonova et al., 2002) have reversible capacities of 350–400 mAh g⁻¹ and 500 mAh g⁻¹, respectively, and Sn-Bi alloy shows better cycling stability. Xiao et al. (2012) synthesized SnSb/C nanocomposite through high energy mechanical milling, and applied SnSb/C nanocomposites as electrodes in SIBs. The coexistence of Sn and Sb phases during the charging/discharging process acted as a self-supporting network while retaining the conductivity of the electrode. The nanocomposite exhibited an initial reversible capacity of 544 mAh g⁻¹ at a current density of 100 mA g⁻¹.

Some elements, such as Fe, Ni, Cu and Co, are electrochemically inactive in Li-ion batteries. When these elements form alloys and intermetallic compounds with Sn like FeSn₂ (Zhang et al., 2008) and applied as electrodes for LIBs, these electrochemically inactive elements do not react with Li. In other words, electrochemically inactive elements confine the sudden volume changes, which improve the cycling performance and rate capability of Sn-based alloys as electrodes. In 1999, Kepler et al. (1999) studied Cu-Sn anodes as anodes in LIBs, and demonstrated that inactive matrix elements utilize the active Sn component. Since then, several investigations have been conducted on this type of Sn-based anode materials. Wang et al. (2010a) synthesized FeSn₂, Ni₃Sn₄, Cu₆Sn₅, and CoSn₃ nanospheres by polyol wet chemistry method and applied them as anodes in LIBs. Among these Sn intermetallics, FeSn₂ shows the best practical reversible capacity, and Ni₃Sn₄ has the worst reversible capacity. The reversible reaction mechanisms for initial lithiation/delithiation are described as:



Xin et al. (2015) studied MSn₅ (M = Fe, Co, and FeCo) intermetallic nanospheres as anodes in LIBs. FeSn₅, CoSn₅, and Fe_{0.35}Co_{0.35}Sn₅ intermetallic showed practical capacities of 750 mAh g⁻¹, 500 mAh g⁻¹, and 736 mAh g⁻¹, respectively, at a discharge current of 0.05C. A C-rate is a measure of the rate at which a battery is charged relative to its maximum capacity. In addition to binary alloys, Sn-based ternary alloys have also been

studied as anodes in rechargeable batteries. Farbod et al. (2014) prepared a variety of Sn-Ge-Sb alloy anodes for SIBs using the co-sputtering method. Sn₅₀Ge₂₅Sb₂₅ presented an excellent specific capacity of 662 mAh g⁻¹ even after 50 cycles at a current density of 8500 mA g⁻¹.

In this section, we have summarized Sn based anode materials for LIBs and their corresponding electrochemical performances. In the following sections, we will discuss the battery properties of anode materials based on nanostructured TiO₂ and its composites with tin. The synthesis method, structure, and battery performance of Sn/TiO₂ based nanomaterials will be critically reviewed and discussed.

3. TiO₂-based anodes

Nanostructured TiO₂ has been considered as an electrode material due to its safe lithiation potential (0.8 V vs. Li/ Li⁺), equivalent capacity (335 mAh g⁻¹ vs 372 mAh g⁻¹ for commercial graphite), and better rate capability. In addition, upon Li ion insertion/extraction process, it presents insignificant volume changes (<4%) and thus minimal structural strain resulting in stability with a long-life cycle (Wang et al., 2015). Nanostructured TiO₂ materials have also been widely studied for environmental applications (Kasinathan et al., 2016; Wang et al., 2017). There are four different TiO₂ polymorphs crystal structure shown in Fig. 1: (a) anatase, (b) rutile, (c) brookite, and (d) TiO₂-B. Among these, the rutile phase is the most thermodynamically stable phase. These TiO₂ nanocrystals have been employed as anode materials in LIBs. The specific capacity of anatase, rutile, brookite and TiO₂-B are 285 mAh g⁻¹ (Aravindan et al., 2015), 210 mAh g⁻¹ (Aravindan et al., 2015), 335 mAh g⁻¹ (Lee et al., 2008) and 225 mAh g⁻¹ (Aravindan et al., 2015) respectively. Rutile TiO₂ displays inferior performance because the ion transport channel is narrow along the c-axis, and the diffusion coefficient in ab plane is nine times less as compared to c plane. However, anatase can provide a higher specific capacity of 285 mAh g⁻¹ by using Li_{0.5}TiO₂. Among TiO₂ polymorphs, TiO₂-B has the highest theoretical specific capacity of 335 mAh g⁻¹ due to its open channel structure, which allows pseudocapacitive Li⁺ storage. In TiO₂-B polymorph, Li⁺ can be accommodated in sites represented as A₁ (scattered in TiO₂ layers equivalent to ab plane), A₂ (scattered in O layers equivalent to ab plane), and C (distributed in indefinite channels along the b axis). These open channels have a significant impact on the diffusion kinetics of Li⁺ and assist their insertion in bulk form.

Although TiO₂ nanostructured electrode materials have small volume changes during charging/discharging, their poor ion mobility and electronic conductivity limits their electrochemical performance (Zhang et al., 2016a). The inferior ion mobility is because of diffusion energy barrier and low electronic conductivity due to wide bandgap. TiO₂ has been employed with materials of high theoretical capacity, such as Sn, SnO₂, Fe₂O₃ and Si etc. as a rigid substrate or backbone to compensate for volume expansion (Lü et al., 2016). In addition, much effort has been attempted to enhance the carrier transport and ion diffusion, including surface engineering, conductive substrate design, carbon coating, and hybridization with a conductive agent.

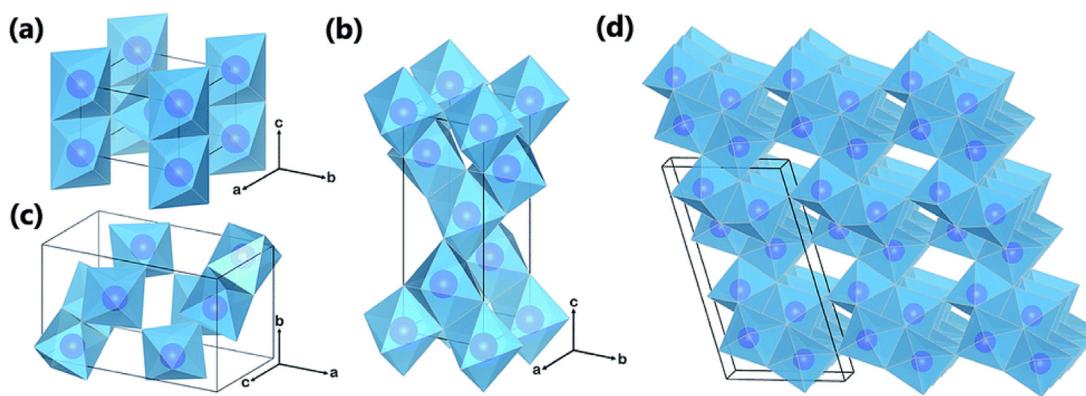


Fig. 1. Crystal structures of TiO_2 polymorphs (a) rutile, (b) anatase, (c) brookite, and (d) $\text{TiO}_2\text{-B}$. Dark colour spheres show the Ti atoms, and light colour octahedra represent TiO_6 blocks (Zhang et al., 2016a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Sn/ TiO_2 based anode materials

Materials like Sn and Si possess much higher theoretical capacities (993 and 4200 mAh g^{-1} respectively) than graphite (372 mAh g^{-1}). However, the application of such electrode materials is restricted by their substantial volume changes during the charging/discharging process and phase transformation in the host material (Shukla and Prem Kumar, 2013). To resolve this critical issue, TiO_2 can be employed as a substrate to modify and enhance the structural stability as discussed in Section 3. In this section, we will review the recent research progress in the synthesis methods and battery characteristics of Sn and TiO_2 based nanocomposites.

Recently, Sn/SnO₂ is integrated into the TiO_2 matrix to achieve structural stability and high energy storage capacity. It is expected that such hybrid nanostructures would retain the high capacity of Sn and structural stability and cycling performance of TiO_2 . Table 2 summarized the methods of synthesis and battery performance of recently reported hybrid nanostructured materials based on Sn and TiO_2 . It can be seen from Table 2 that a wide range of Sn and TiO_2 nanostructured materials have been synthesized and studied as electrodes for LIBs. High battery capacities are achieved at high current density, such as 1044 mAh g^{-1} at 100 mA g^{-1} , but the cycling performance is low. Among these studies, hydrothermal process—a solution-processed technique is most widely used. Based on the structure of nanocomposites, they can be categorized into four groups:

- i. Sn doped TiO_2 nanostructure
- ii. Sn/ TiO_2 core-shell nanostructure
- iii. 3D porous structure
- iv. Other nanocomposite structures

The characteristics and mechanisms involved for each category will be discussed in the following sections.

4.1. Sn doped TiO_2 nanostructure

Doping induces variation in the electronic structure and intrinsic properties, impacting the interface chemical reactions, hence controlling the overall electrochemical performance. It will therefore regulate the electron transfer process and provides additional channels for Li^+ diffusion because of modification in the lattice structure (Kumar et al., 2020). In 2014, Yu et al. (2014) modified the electrical conductivity of anatase TiO_2 nanotubes by Sn doping, employing sol-gel and hydrothermal processes. These authors varied the Sn content in the doping process that caused

an increase in electrical conductivity due to increased charge carriers and Hall mobility. The morphology of pristine and Sn doped TiO_2 nanotubes are illustrated in Fig. 2(a, b). The charge/discharge profiles of pristine anatase TiO_2 and 5% doped samples, as shown in Fig. 2 (c, d), illustrate the initial lithiation/delithiation capacity of 342 and 252 mA gh^{-1} and a coulombic efficiency of 73.68%. Furthermore, 5% Sn doping gave the maximum capacity of 386 mAh g^{-1} at 0.1C after 50 cycles and a columbic efficiency of 99.2%. The cycling performance results are compared in Fig. 2(e).

In 2015, Lübeck et al. (2015) synthesized Sn doped TiO_2 nanoparticles by continuous hydrothermal flow synthesis reactor and applied in LIBs assembly immediately. The increasing Sn concentration affected the surface area and enhanced crystallite size ultimately reducing the ionic diffusion. In a wider potential range (0.05–3V vs Li/Li⁺), Sn doped TiO_2 outperformed and resulted in a specific capacity of 350 mAh g^{-1} at 100 mA g^{-1} for 500 cycles. Similarly, Jiao et al. (2018) doped Sn into rutile TiO_2 nanocrystals by template-free hydrothermal process and reported a specific capacity of 251.3 mAh g^{-1} at 0.1 A g^{-1} for 150 cycles and after 500 cycles, it retained the reversible capacity of 110 mAh g^{-1} at 5 A g^{-1} .

In 2016, Zeng et al. (2016) designed C-NS/ TiO_2 by doping nano-Sn into carbon-coated TiO_2 using the sol-gel method. These researchers reported that the carbon layer contained Sn expansion, the TiO_2 maintained the electrode structural integrity and nano-Sn provided high reversible capacity. After 200 cycles, the working electrode was able to give a reversible capacity of 219 mAh g^{-1} at a current density of 500 mA g^{-1} . The outer layer of carbon and inner TiO_2 spheres formed a monodisperse matrix with nano-Sn that contributed to achieving higher discharge capacity.

4.2. Sn/ TiO_2 core-shell nanostructure

Another widely applied strategy is to fabricate core-shell nanostructures. Core-shell nanostructure materials consist of two different components in which one acts as an inner core structure and the other as the outer shell, exhibiting unique properties based on different materials, geometry, and design (El-Toni et al., 2016). Such a unique nanostructure possesses the following advantages:

- a. Modified/controlled physical and chemical properties,
- b. The shell provides a shield to primary core materials from external changes,
- c. Sustained structural stability and limits volume expansion,
- d. Restraining the aggregation of core material,
- e. Controlled access of ions and molecules to the core.

Table 2Sn/TiO₂ hybrid nanocomposites as anode materials for LIBs.

Anode Material and its structure	Synthesis Method	Battery Cycling performance			Ref.
		Discharge Capacity (mAh g ⁻¹)	Current Density (mA g ⁻¹)	No of cycles	
Sn doped rutile TiO ₂ hollow nanocrystals	Hydrothermal process	110	5000	500	Jiao et al. (2018)
Sn doped TiO ₂ nanotubes	Sol-gel and hydrothermal process	386	0.1C	50	Yu et al. (2014)
Sn doped and carbon coated rutile TiO ₂ spheres	Sol-gel method	219	500	200	Zeng et al. (2016)
Sn doped TiO ₂ thin films	Spin coating followed by pyrolysis process	252.5	84	80	Wang et al. (2013a)
SnO ₂ /TiO ₂ embedded in porous Carbon	Solvothermal method	1044	100	100	Shi et al. (2017)
SnO ₂ @TiO ₂ core-shell nanostructure	Hydrothermal method and atomic layer deposition	703	80	50	Chen et al. (2019a)
TiO ₂ @Sn core-shell nanotubes	Hydrothermal method	176	4000	60	Kim et al. (2008)
SnO ₂ @TiO ₂ core-shell	Sol-gel method	910	100	300	Yi et al. (2016)
Yolk-like SnO ₂ @ TiO ₂ nano-spheres	Hydrothermal method	472.7	2000	800	Tian et al. (2017a)
Rutile TiO ₂ @ SnO ₂ nanorods/carbon cloth	Hydrothermal	700	100	100	Liu et al. (2020)
Double shell SnO ₂ @amorphous TiO ₂	Wet chemistry method	334	100	50	Yang et al. (2017a)
SnO ₂ @TiO ₂ C hetero nanostructures	Hydrothermal method	676	200	50	Tian et al. (2017b)
3D SnO ₂ @TiO ₂ spheres encapsulated in reduced graphene oxide	Hydrothermal method	668.2	100	200	Xin et al. (2019)
Mesoporous SnO ₂ @C@TiO ₂ nano-chains	Hydrothermal method	369	100	100	Luo et al. (2015)
Hollow SnO ₂ /TiO ₂ nanostructures	Template assisted deposition	700	156.4	50	Peng et al. (2000)
Hollow TiO ₂ @SnO ₂ @ carbon nanobelts	Hydrothermal method	804.6	200	500	Tian et al. (2018a)
Multi-layered hollow TiO ₂ @SnO ₂ @C spheres	Hydrothermal method	484	200	300	Wang et al. (2020a)
SnO ₂ @TiO ₂ double nano-shells in graphene nanoribbons	Chemically unzipping method	536	3000	1500	Li et al. (2016a)
C encapsulated SnO ₂ @graphene/TiO ₂ nanocomposite	Hydrothermal method	524	500	200	Li et al. (2014)
Sn-SnO ₂ @CNT nanocomposite	Hydrothermal method	744	500	1000	Sun et al. (2019)
Nanostructured Sn/TiO ₂ /C composite	Mechanochemical reduction method	610	100	100	Park et al. (2009)
C-TiO ₂ -SnO ₂ nanocomposite	Sol-gel method	378	30	40	Zhou et al. (2012)
3D TiO ₂ -SnO ₂ composite	Thermal convection hydrothermal method	448.3	500	500	Chao et al. (2020)
TiO ₂ /SnO ₂ /C composite	Hydrothermal method	492.4	1000	400	Tian et al. (2018b)
TiO ₂ /1D SnO ₂ nanotubes	Electrospinning	522.3	5000	250	Cheong et al. (2018)
TiO ₂ @SnO ₂ nanotubes	Electrospinning and sol-gel method	438.3	5000	80	Cheong et al. (2017a)
Pipe wire TiO ₂ -Sn@carbon nanofibers	Electrospinning and atomic layer deposition	634	200	1100	Mao et al. (2017)
SnO ₂ /TiO ₂ nanofibers	Electrospinning	560	100	80	Tran et al. (2014)
Sn NPs in TiO _{2-x} nanofibers	Heat assisted electrospinning	957	100	200	Li et al. (2016b)
TiO ₂ -Sn/C nanofibers in sodium ion batteries	Electrospinning	118.1	5000	2000	Nie et al. (2018)
Super small TiO ₂ /SnO ₂ /Sn/C nanohybrids	Wet chemistry method	452	200	400	Wang et al. (2020b)
SnO ₂ @TiO ₂ Ns@C nanospheres	Hydrothermal method	642.5	1000	450	Bao and Tian (2018)
TiO ₂ /SnO ₂ /C nanospheres	Hydrothermal method	687.2	200	400	Tian et al. (2018c)
Carbon coated TiO ₂ /SnO ₂ nanospheres	Hydrothermal	576.1	200	500	Tian et al. (2018d)
SnO ₂ @TiO ₂ hollow spheres	Template assisted approach	264.8	170	100	Chen et al. (2010)
SnO ₂ and TiO ₂ Multi shell microspheres	Solvothermal method	1045	100	650	Jiang et al. (2019a)
Sphere like SnO ₂ /TiO ₂	Spray drying followed by thermal treatment	483	500	40	Li et al. (2019)
SnO ₂ modified hollow TiO ₂ nanoarchitecture	Topotactic synthetic method	213	170	100	Jia et al. (2018)
Carbon riveted 2D@ODTiO ₂ nanosheets@SnO ₂ nanoparticles	Phase transformation strategy	474	1000	650	Tian et al. (2020)
Self-organized TiO ₂ @SnO ₂ nanoparticles	Hydrothermal and pyrolysis method	834	200	100	Li et al. (2018a)

Note: CNT: carbon nanotube.

The core–shell nanostructures can shorten the Li⁺ diffusion length for insertion/extraction by providing alternative electron transport paths, accelerating the charge transfer at the electrode/electrolyte interface, and enhancing the conductivity and reactivity of Li⁺ (Su et al., 2011). Fig. 3 shows the synthesis process, the high-resolution transmission electron microscopy (HRTEM) image and battery cycling performance of core–shell SnO₂@TiO₂ nanocomposite.

Another group of researchers prepared a yolk like structure, in which TiO₂ not only provided mechanical support to SnO₂ but also prevented the pulverization and aggregation during the Li⁺ insertion/extraction process as well as contributed to the overall capacity (Tian et al., 2017a). In addition, the mesoporous structure offered high contact area between electrode and electrolyte and expedited diffusion of both electron and Li⁺, eventually achieving a specific capacity of 518.2 mAh g⁻¹ at a current density of 800 mA g⁻¹ over 500 cycles.

To synthesis porous core–shell structures, hydrothermal method has been widely used. For instance, Liu et al. (2020)

synthesis a core branched nanostructure (r-TiO₂-NRs @ r-SnO₂-NRs) and applied in LIBs assembly. This nanostructure is based on SnO₂ nanorods as a shell and rutile TiO₂ nanorods as a core, grown vertically on a flexible carbon cloth. This structure resulted in a discharge capacity of 700 mAh g⁻¹ at 0.1 A g⁻¹ and a capacity retention of 86% after 100 cycles. Chen et al. (2019b) designed a core–shell structure in which crystalline SnO₂ acts as a core matrix and amorphous TiO₂ as a shell by hydrothermal and atomic layer deposition methods. The core–shell structure gave high conductivity to the SnO₂ electrode, leading to contact improvement between electrode and electrolyte. In addition, Zhang's group fabricated a porous core shell-structure of SnO₂/TiO₂ composite by a photo deposition method (Wang et al., 2013a). SnO₂ nanoparticles were photo deposited on hydrogenated TiO₂ nanotubes (H-TiO₂). Fig. 4-b shows a view of vertically aligned free-standing nanotubes. This porous core–shell structure acts as a bamboo structure, exposing a large surface area and photoactive sites, imparting high electronic and ionic conductivities, and fast kinetics.

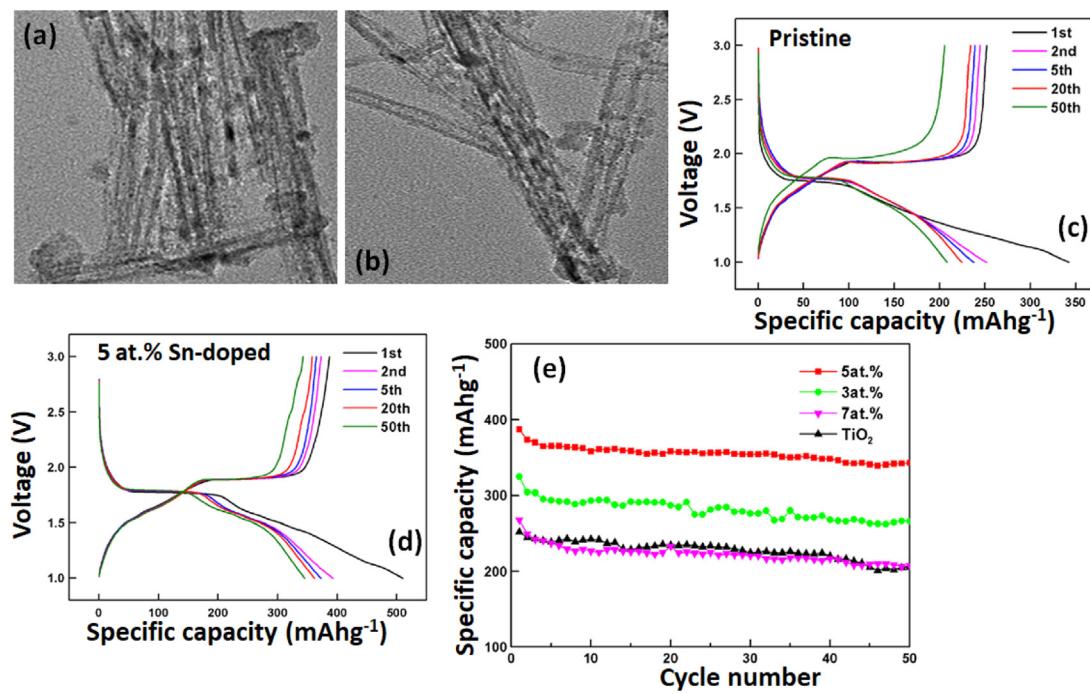


Fig. 2. TEM images of (a) pristine and (b) 5 at.% Sn doped TiO₂ nanotubes, bar scale is 50 nm. Initial charge/discharge profiles of (c) pristine and (d) 5% doped sample, (e) Cycling performance comparison of pristine and Sn doped samples (Yu et al., 2014).

4.3. 3D porous nanostructure

Design and synthesis of Sn/TiO₂ based 3D nanostructure materials is also an effective method to contain the uncontrolled volume expansion of Sn. In addition, Sn/TiO₂ based 3D nano-materials possess the advantages of large internal void spaces, and/or establish electric conduction networks, providing multiple paths for electron/ion transport, and a large surface area, which enhance their electrochemical performance in LIBs. Li et al. (2018b) fabricated a 3-dimensional structure by a combination of hydrothermal and pyrolysis method, and denoted the product as TiO₂@SnO₂. As prepared, self-organized 3D nanostructure has resulted in a charge storage capacity of 834 mAh g⁻¹ at a current density of 200 mA g⁻¹ for 100 cycles and a capacity retention of 120%. The 3D structure acted as a barrier for SnO₂ nanoparticles to agglomerate, and TiO₂ nano network provided the buffering space to counter pulverization, porous structure enhanced electrolyte infiltration, ultimately bringing stability and high electrochemical performance.

In a similar manner, 3D carbon is coated on TiO₂/SnO₂ nanospheres in a tussocky manner to form 3D nanostructured TiO₂@SnO₂@3DC (Tian et al., 2018d). This structure improved charge transfer capacity and enhanced surface contact between anode material and electrolyte, achieving a reversible capacity of 576.1 mAh g⁻¹ and columbic efficiency of 99.7% at 200 mA g⁻¹ after 500 cycles. Similarly, Yang et al. (2017b) applied the morphology control approach and prepared double-shell

SnO₂@amorphousTiO₂ hollow nanospheres, which showed a specific capacity of 334 mAh g⁻¹ at 100 mA g⁻¹ after 50 cycles.

Chao et al. (2020) applied a different approach and utilized cationic surfactant (cetyltrimethylammonium bromide (CTAB)) instead of C coating for uniform distribution of SnO₂ nanoparticles on TiO₂ substrate. CTAB provided morphology control using electrostatic forces between SnO₂ and CTAB in a reaction solution that uniformly distributed SnO₂ nanoparticles. As a result, it devised a hierarchical porous 3D nanostructure with ample surface area and assisted in Li⁺ storage. The composite made

use of the synergistic effects of both TiO₂ microclews (TiO₂ MCs) and SnO₂ and resulting in ultra-high ion transport. The prepared structure (CA-TiO₂@SnO₂ MCs) showed a reversible charge capacity of 448.3 mAh g⁻¹ at a current density of 500 mA g⁻¹ after 500 cycles (Chao et al., 2020).

4.4. Other nanocomposite structures

Apart from the strategies discussed, various other schemes have been studied to devise Sn and TiO₂ based nano-architectures, including nanoparticles, nanotubes, nanowires, nanospheres, nanofibers, and nanorods. These are summarized in Table 2 under the column headed “Electrode Material”, highlighting active electrode material structure and their key battery performance parameters.

Nanoarrays, especially nanowires and nanotubes, are self-supported structures and have the capacity to transfer charges quickly and they also have ample void spaces to contain Sn volume expansion. Thus, Wei et al. (2013) made use of the advantages of TiO₂ nanowire arrays (TNA) and Sn in a nanocomposite denoted as TNA/Sn. The TNA/Sn nanocomposite showed an initial volumetric capacity of 1610 mAh cm⁻³ and retained 1006 mAh cm⁻³ after 300 cycles, four folds higher than TNA. They attributed this high cycling performance to the crystal growth direction of nanowires and an increase in electrical conductivity. Equally, Tian et al. (2020) combined the synergetic effect of TiO₂, SnO₂ and carbon and applied nanocomposite (TiO₂NSs@SnO₂@C) as an anode in LIBs. The novel nanostructure resulted in an excellent electrochemical kinetics and structural stability, which achieved a high storage capacity of 758 mAh g⁻¹ at 200 mA g⁻¹ for 390 cycles and 474 mAh g⁻¹ at 1000 mA g⁻¹ after 650 cycles.

In addition, a template-free solvothermal method was applied to prepare multi-shell microspheres of SnO₂ and TiO₂ (Jiang et al., 2019b). The structure and chemical composition of microspheres is controlled by the reaction time. The prepared microspheres achieved high discharge capacity of 1045 mAh g⁻¹ at a current density of 0.1 A g⁻¹ even after 650 cycles. Similarly, Shi et al. (2017) applied the solvothermal method and utilized a

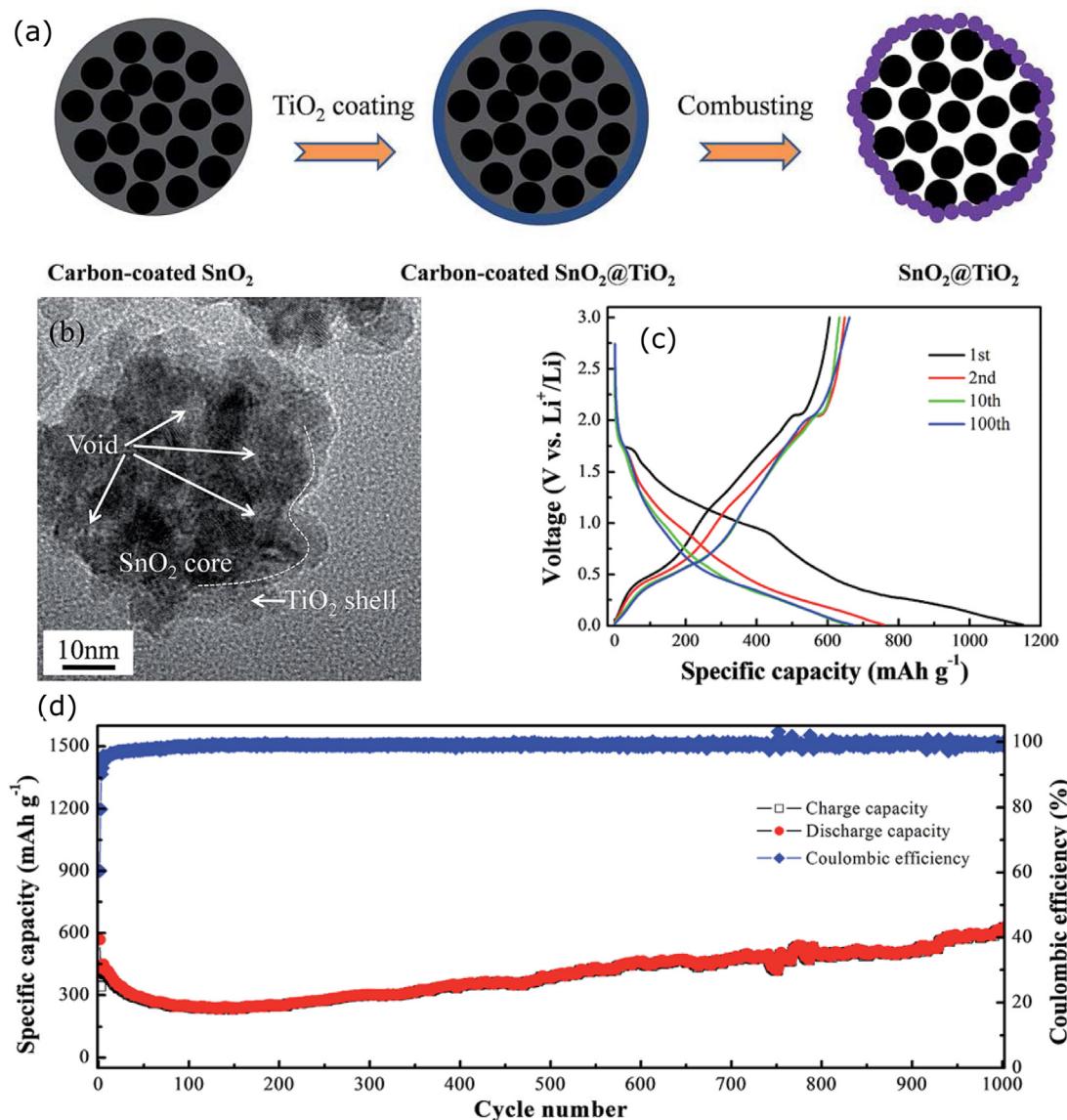


Fig. 3. (a) Schematic of the synthesis of core-shell SnO₂@TiO₂ nanocomposite. (b) HRTEM of SnO₂@TiO₂, (c) charge/discharge curves of core-shell SnO₂@TiO₂ at a current density of 100 mA g⁻¹, (d) galvanostatic charge/discharge cycle performances at a current density of 1000 mA g⁻¹. (Yi et al., 2016).

metal-organic framework (MIL125) as a source of C and TiO₂ and prepared unique Eccles cake morphology (SnO₂/TiO₂/C) composite. They reported that the nanocomposite has high capacity of 1045 mAh g⁻¹ at a current density of 100 mA g⁻¹ after 100 charge-discharge cycles, which due to SnO₂ NPs delivered major energy storage capacity, whereas TiO₂, combined with C, stabilized the structure.

5. Hybrid approach

It can be seen from Table 2 that electrodes of nanocomposites based on metal oxides such as TiO₂, and Sn transition metals exhibit high electrochemical performance for batteries. Hybrid nanostructure materials are a combination of two or more components at nanoscale having unique properties (Nanko, 2009). Physical/chemical compatibility of individual components and their interfacing abilities are necessary characteristics for the development of hybrid nanostructured materials. Thus, suitable design and controlled synthesis of such materials can be employed to fine-tune the material properties and functions (Povolotskaya et al., 2015) as represented in Fig. 5. Compared to bulk materials,

hybrid nanostructure materials improve the electrode/electrolyte interface with high contact area, thus facilitating the transfer of high power and energy densities. As discussed in Section 4, Sn/TiO₂ based hybrid nanostructures have demonstrated that hybrid nano architectures can improve the storage capacity and structural stability and minimize the pulverization issues arising from Sn drastic volume fluctuations.

Table 3 summarizes the structure, synthesis method, and battery cyclic properties of other recent developed anode materials. The first part of Table 3 lists anode materials with one component. Although the battery performance enhanced using carbon nanotubes or graphene nanosheets as anode materials in LIBs, the battery capacity is still lower than 500 mAh g⁻¹. The second part of Table 3 summaries the structure, synthesis method and battery properties of recent developed hybrid nanostructures as anode materials for LIBs. Compared to Sn/TiO₂ hybrid nanomaterials (Table 2), the latest invented hybrid nanostructure materials, such as graphitic carbon nitride/Mo₂CT_x (g-C₃N₄/Mo₂CT_x) (Wan et al., 2021), self-healing gallium phosphide TiO₂-C (GaP@TiO₂-C) (Huy et al., 2021), and silicon nanocrystal-micro carbon ball (SN-MCB) (Kwon et al., 2020), shows superb

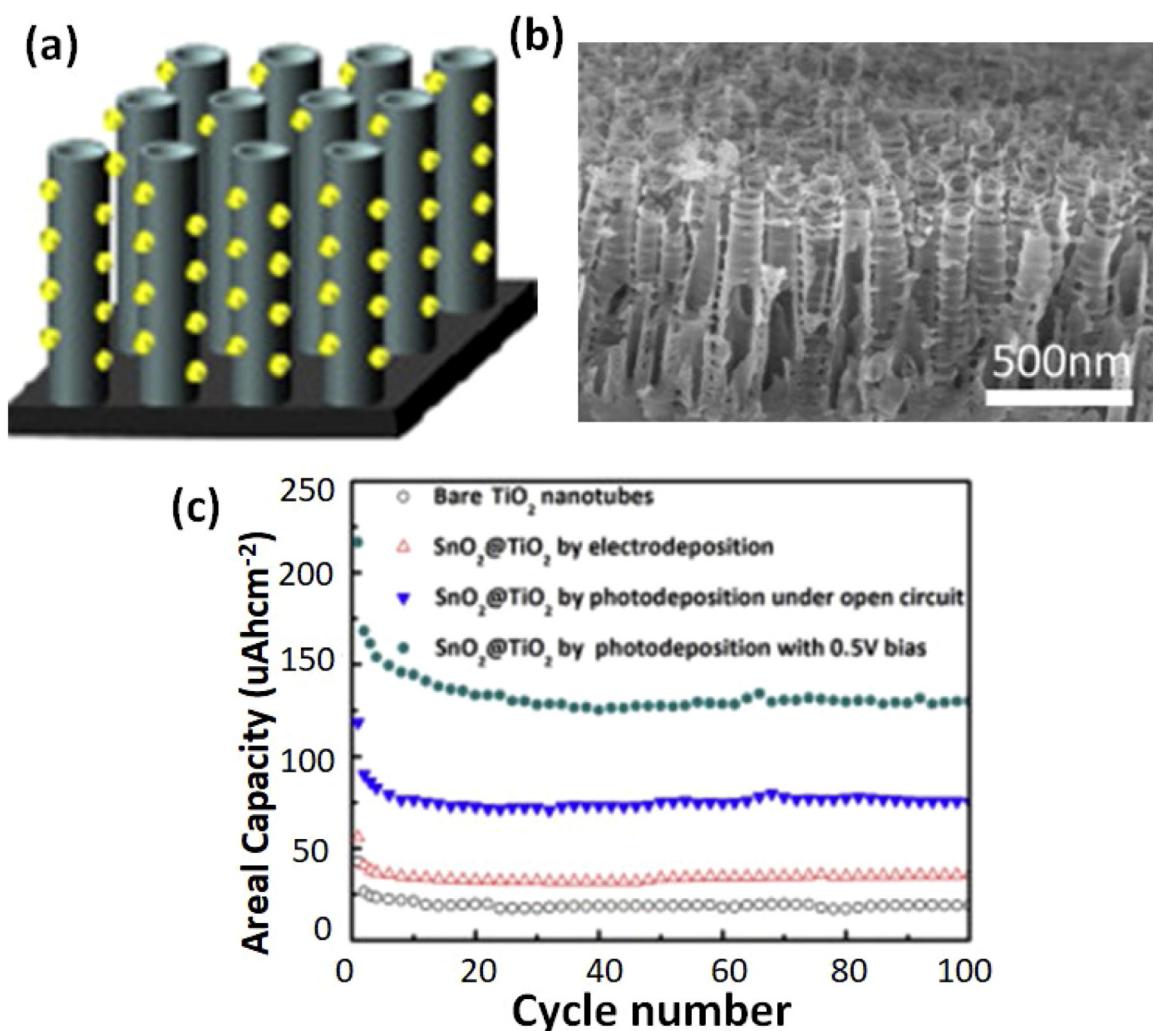


Fig. 4. (a) The layout of synthesized $\text{SnO}_2/\text{TiO}_2$ nanocomposite, (b) Cross-sectional view of SEM image, and (c) Cycling performance comparison of bare TiO_2 and $\text{SnO}_2/\text{TiO}_2$ nanocomposite at different potential biases (Zhang et al., 2016b).

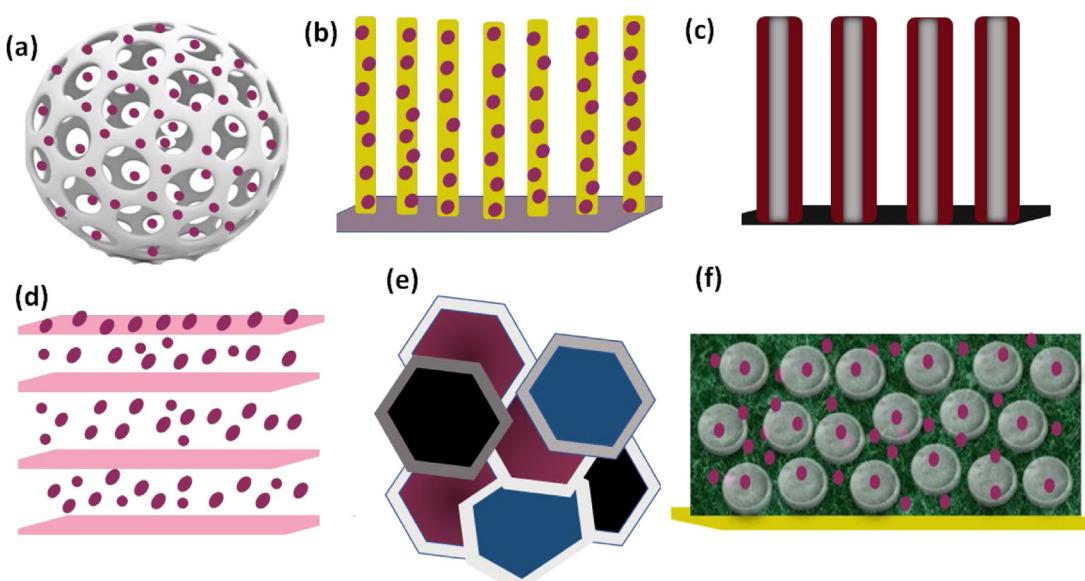


Fig. 5. Explanation of hybrid nanostructure materials, (a) 0D: nanodots enclosed in hollow nanospheres, (b–c) 1D: nanowire arrays, (d–e) 2D: coated or doped 2D nanomaterials, (f) 3D: porous composite (Mohamed, 2017).

Table 3

Summary of structure, preparation method, and electrochemical performance of recent developed anode materials with and without hybrid nanostructure.

Anode Material	Synthesis Method	Battery Cycling performance			Ref.
		Discharge Capacity (mAh g ⁻¹)	Current Density (mA g ⁻¹)	No of cycles	
Anode materials with single component					
Carbon nanotubes	Pulsed laser vaporization	460	20		Claye et al. (2000)
Graphene nanosheets	Modified Hummers method	478	200	100	Wan et al. (2011)
Carbon nanospheres	MOCVD	400	186	100	Huang et al. (2016)
N-doped reduced GO	Modified Hummers method	240	10 000	500	Tasdemir et al. (2021)
Nb ₂ O ₅ nanosheets	Hydrothermal	117	200	100	Liu et al. (2015)
Nb ₂ O ₅ nanofibers	Electrospinning	~160	500	2000	Cheong et al. (2017b)
ZnV ₂ O ₄ nanowires	Hydrothermal method	460	1000	100	De Juan-Corpuz et al. (2019)
Hybrid nanostructure anode materials					
GQD@CNTs	Hydrothermal method	700	100	100	Zhao et al. (2020)
GeO _x /Graphene	In situ chemical synthesis	1110	200	50	Wei and Guo (2013)
GeO _x @C core-shell	Coaxial electrospinning	875	160	400	Li et al. (2015)
Co ₃ V ₂ O ₈ /rGO	Hydrothermal method	1050	50	200	Gao et al. (2016b)
Zn ₃ V ₂ O ₈ /GNPs	Liquid reflux and calcination	648	800	100	Bie et al. (2017)
ZnO@C nanocomposite	Pyrolysis	932	100	100	Fu et al. (2017)
MnO@C microspheres	Wet chemical method	596.3	3825	1000	Cui et al. (2017)
Porous MnO/C NTs	Hydrothermal process	763.3	100	100	Xu et al. (2012)
CuO/C microcubes	Pyrolysis process	510.5	100	200	Yin et al. (2017)
GaP@TiO ₂ -C	Milling	1012	500	500	Huy et al. (2021)
g-C ₃ N ₄ /Mo ₂ CT _x MXene	HF Etching	528.5	100	100	Wan et al. (2021)
NiCoO _x @C microspheres	Hydrothermal process	511.7	500	200	Yi et al. (2021)
Fe ₃ O ₄ /Fe ₇ S ₈ @C composite	Rheological phase method	819	1000	300	Hai Tian et al. (2020)
MoS ₂ coated MoO ₂	Roasting precursors	1052	200	150	Sun et al. (2021)
CNTs@Mn ₃ O ₄	Solution processing	895	500	200	Cao et al. (2021)
FeS@TiO ₂ nanocomposite	Hydrothermal method	510	200	100	Wang et al. (2013c)
Co ₃ O ₄ /TiO ₂ heterostructure	Electrospinning	602.8	200	480	Wang et al. (2012b)
TiO ₂ -C/MnO ₂ core double shell nanowires	Layer-by-layer deposition	332	670	100	Liao et al. (2013)
TiO ₂ @Fe ₂ O ₃ hollow structure	Atomic layer and hydrolysis method	530	200	200	Luo et al. (2013)
ZnO@C:N	Precursors carbonization	608	100	500	Guo et al. (2020)
ZnO@C nanocrystals	Coprecipitation method	818	100	50	Fan et al. (2017)
Si nanowires @G@rGO	CVD and annealing	1280	2100	100	Wang et al. (2013b)
C@porous Si/rGO composite	Pyrolysis	743	400	100	Ding et al. (2021)
Ge/N-C (N doped carbon embedded Ge NPs)	Sol-gel method	1042	800	2000	Ma et al. (2017)
Ge-na/C NN NWs	MOCVD	933	1623	1000	Lee et al. (2015)
Mesoporous hollow Ge@C	One pot method	1285	320	200	Li et al. (2013)
SnS ₂ /Sn ₃ S ₄ decorated Ti ₃ C ₂	Solvothermal followed by Calcination	462.3	100	100	Li et al. (2020)
SnO ₂ @MoO ₃ @graphene	Hydrothermal and ball milling	1522.5	200	250	Deng et al. (2021)
N-doped G@Si@hybrid silicate	CVD	817	21 000	10 000	Huang et al. (2020)
Si-C hybrid composite	Micro-emulsion method	1800	10	500	Kwon et al. (2020)
Si@graphite@C composite	CVD	~710	0.2C	200	Zhu et al. (2021)

Note: MOCVD: metal–organic chemical vapour deposition.

GO: graphene oxide; and rGO: reduced graphene oxide.

G: graphene.

CVD: chemical vapour deposition.

electrochemical properties and battery cyclic performance as anodes in LIBs (**Table 3**). Hybrid nanostructures with carbon and other conductive materials facilitates ionic and electronic conductivity, thus providing a steady flow of electrons to redox sites and ultimately leads to improvement in energy storage and cyclic performance of batteries (Hwang et al., 2011). For example, carbon-coated hybrid microspheres (ZnO@C) shows a much higher discharge capacity of 818 mAh g⁻¹ than the capacity of solid ZnO (510 mAh g⁻¹) at the current density of 0.1 A g⁻¹. Because the porous structure possesses a large surface area, fast charge transport capability and enough space to accommodate volume changes (Zhao et al., 2017). Hybrid materials also contain high surface energy due to surface dangling bonds (Dai et al., 2016).

Furthermore, hybrid structures are mechanically stable and prevent the structural imbalance and phase changes to the electrodes as well as regulate the volumetric changes because of their tuneable structures (Simon et al., 2014). Kwon et al. (2020)

demonstrated a unique nano/microstructured Si-C hybrid composite comprised of silicon nanoparticles embedded in micron-sized amorphous carbon balls, denoted as SN-MCB (silicon nanocrystal-micro carbon ball). The synthesis process and electrochemical properties are shown in Fig. 6. This hybrid structure provides high electronic conductivity and significantly decreases the absolute stress/strain of the material during lithiation-delithiation processes. Therefore, the Si-C hybrid composite anode shows a high capacity of 1800 mAh g⁻¹, outstanding cyclic stability with capacity retention of 80% over 500 cycles, and fast charge-discharge capability of 12 min.

6. Conclusion and outlook

Due to high theoretical capacity and environmental friendliness, Sn has been considered a promising candidate as a negative electrode for next-generation LIBs. However, uncontrolled volume changes during the charging/discharging affect its cycling stability and restrict commercial applications. TiO₂ has insignificant volume changes (<4%) during lithiation/delithiation, but it

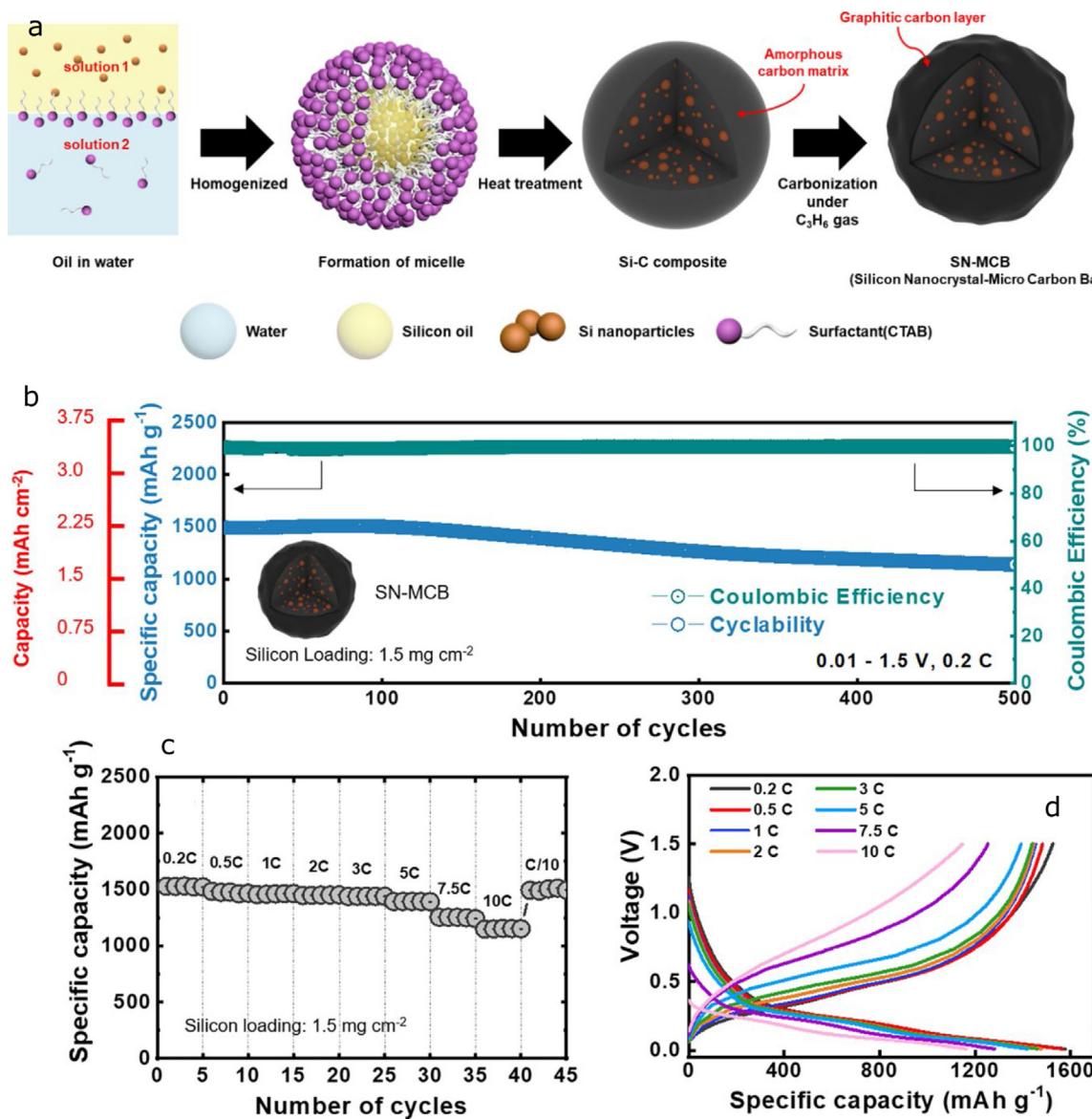


Fig. 6. (a) Schematic showing the synthesis process of Si-C hybrid nanostructure material. (b) Long-term cycling stability of the SN-MCB anode in a half-cell at 0.2 C. (c) Rate capability test and (d) corresponding voltage profiles between 0.1 and 10 C. The electrochemical measurements were tested in a voltage range of 0.01–1.5 V at 30 °C.

suffers from poor electrical conductivity and ion mobility. In this article, we have discussed the practical strategies that have been explored to enhance the electrochemical performance of Sn and TiO₂ based nanocomposite materials. Then, we have emphasized a hybrid approach for designing and synthesizing high-performance electrode materials for LIBs. Hydrothermal process is mainly used as synthesis method for preparing hybrid nanostructure materials. Recent researches emphasized on engineering various hybrid nano architectures to improve the storage capacity, structural stability and minimizing pulverization issues arising from Sn drastic volume changes. Energy density of Sn/TiO₂ based hybrid nanostructures have shown a significant improvement from 200 mAh g⁻¹ to 1044 mAh g⁻¹ at the current density of 100 mA g⁻¹, but they still suffer in terms of cycling stability.

The latest developments on hybrid nanostructures with carbon and other conductive materials significantly improve the

battery cycling performance of LIBs. In addition, layered materials, such as Xenes, MXenes, and transition metal chalcogenides (TMCs), show high electrochemical activity and exceptional chemical properties. The design and development of MXenes or TMCs based hybrid nanostructure materials offer great opportunities to achieve high performance LIBs. Furthermore, self-healing liquid metal electrodes, for instance, Ga-based electrodes, have demonstrated ultra-long cycling properties, but suffer from low capacity. Design and develop new hybrid nanostructures with combining self-healing alloys and high capacity nanomaterials could enhance the energy density and cyclic performance of LIBs.

Nevertheless, there is a need to develop a facile, controlled, and economical approach on a large scale to synthesize hybrid nanostructures with stable, tuneable, and highly reversible conversion reactions. We foresee that this review article will inspire researchers to develop a scalable and low-cost fabrication method for designing and engineering high-performance hybrid nanostructure materials as anodes in LIBs with high energy density and long-cycle life.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful to NZ Product Accelerator, a Ministry of Business, Innovation & Employment (MBIE), New Zealand funded programme for financial support of this work under Grant UOAX 1309. Dr. Shanghai Wei also wishes to thank the Marsden Fund Council, New Zealand, managed by Royal Society Te Apārangi, of Fast-Start Marsden Grant via project no. UOA1817.

References

- Anon, 2019. Battery revolution to evolution. *Nat. Energy* 4, 893, <https://doi.org/10.1038/s41560-019-0503-2>.
- Aravindan, V., Lee, Y.S., Yazami, R., Madhavi, S., 2015. TiO₂ polymorphs in 'rocking-chair' Li-ion batteries. *Mater. Today* 18 (6), 345–351.
- Asanithi, P., Chaiyakun, S., Limsuwan, P., 2012. Growth of silver nanoparticles by DC magnetron sputtering. *J. Nanomater.* 2012.
- Asenbauer, J., Eisenmann, T., Kuenzel, M., Kazzazi, A., Chen, Z., Bresser, D., 2020. The success story of graphite as a lithium-ion anode material—fundamentals, remaining challenges, and recent developments including silicon (oxide) composites. *Sustain. Energy Fuels* 4 (11), 5387–5416.
- Bao, D., Tian, Q., 2018. Interconnected quasi-nanospheres of SnO₂/TiO₂/C with gap spaces for improved lithium storage. *Mater. Lett.* 229, 48–52.
- Bie, C., Pei, J., Wang, J., Hua, K., Chen, D., Chen, G., 2017. Graphite nanoplates firmly anchored with well-dispersed porous Zn3V2O8 nanospheres: Rational fabrication and enhanced lithium storage capability. *Electrochim. Acta* 248, 140–149.
- Cao, K., Jia, Y., Wang, S., Huang, K.J., Liu, H., 2021. Mn₃O₄ Nanoparticles anchored on carbon nanotubes as anode material with enhanced lithium storage. *J. Alloys Compd.* 854.
- Chao, M., et al., 2020. Facile synthesis of CTAB assisted hierarchical-structure TiO₂@SnO₂ for lithium storage. *Solid State Sci.* 100 (January).
- Chen, J.S., Luan, D., Li, C.M., Boey, F.Y.C., Qiao, S., Lou, X.W., 2010. TiO₂ And SnO₂@TiO₂ hollow spheres assembled from anatase TiO₂ nanosheets with enhanced lithium storage properties. *Chem. Commun.* 46 (43), 8252–8254.
- Chen, H., et al., 2019a. Crystalline SnO₂ @ amorphous TiO₂ core–shell nanostructures for high-performance lithium ion batteries. *Electrochim. Acta* 310, 203–212.
- Chen, H., et al., 2019b. Crystalline SnO₂ @ amorphous TiO₂ core–shell nanostructures for high-performance lithium ion batteries. *Electrochim. Acta* 310, 203–212.
- Cheong, J.Y., et al., 2017a. Revisiting on the effect and role of TiO₂ layer thickness on SnO₂ for enhanced electrochemical performance for lithium-ion batteries. *Electrochim. Acta* 258, 1140–1148.
- Cheong, J.Y., et al., 2017b. Mesoporous orthorhombic Nb₂O₅ nanofibers as pseudocapacitive electrodes with ultra-stable Li storage characteristics. *J. Power Sources* 360, 434–442.
- Cheong, J.Y., et al., 2018. Incorporation of amorphous TiO₂ into one-dimensional SnO₂ nanostructures as superior anodes for lithium-ion batteries. *J. Power Sources* 400 (February), 485–492.
- Cho, Y.J., et al., 2013. Germanium-tin alloy nanocrystals for high-performance lithium ion batteries. *Phys. Chem. Chem. Phys.* 15 (28), 11691–11695.
- Chung, B.X., Liu, C.P., 2004. Synthesis of cobalt nanoparticles by DC magnetron sputtering and the effects of electron bombardment. *Mater. Lett.* 58 (9), 1437–1440.
- Claye, A.S., Fischer, J.E., Huffman, C.B., Rinzler, A.G., Smalley, R.E., 2000. Solid-state electrochemistry of the li single wall carbon nanotube system. *J. Electrochem. Soc.* 147 (8), 2845.
- Cui, Z., et al., 2017. A new strategy to effectively alleviate volume expansion and enhance the conductivity of hierarchical MnO₂@C nanocomposites for lithium ion batteries. *J. Mater. Chem. A* 5 (41), 21699–21708.
- Dai, R., Sun, W., Wang, Y., 2016. Ultrasmall tin nanodots embedded in nitrogen-doped mesoporous carbon: Metal-organic-framework derivation and electrochemical application as highly stable anode for lithium ion batteries. *Electrochim. Acta* 217, 123–131.
- De Juan-Corpuz, L.M.Z., et al., 2019. Porous ZnV₂O₄ nanowire for stable and high-rate lithium-ion battery anodes. *ACS Appl. Nano Mater.* 2 (7), 4247–4256.
- Deng, X., et al., 2021. Synthesis and electrochemical performances of ternary nanocomposite SnO₂@MoO₃@graphene as high-performance anode material for lithium-ion batteries. *Chem. Phys. Lett.* 770 (February), 138408.
- Ding, N., et al., 2021. Pomegranate structured C@pSi/rGO composite as high performance anode materials of lithium-ion batteries. *Electrochim. Acta* 367.
- Divakaran, A.M., et al., 2020. Rational design on materials for developing next generation lithium-ion secondary battery. *Prog. Solid State Chem.* 100298.
- El-Toni, A.M., et al., 2016. Design, synthesis and applications of core–shell, hollow core, and nanorattle multifunctional nanostructures. *Nanoscale* 8 (5), 2510–2531.
- Fan, H., et al., 2017. From zinc-cyanide hybrid coordination polymers to hierarchical yolk-shell structures for high-performance and ultra-stable lithium-ion batteries. *Nano Energy* 33 (October 2016), 168–176.
- Farbod, B., et al., 2014. Anodes for sodium ion batteries based on tin-germanium-antimony alloys. *ACS Nano* 8 (5), 4415–4429.
- Fu, Y., et al., 2017. Porous ZnO@C core–shell nanocomposites as high performance electrode materials for rechargeable lithium-ion batteries. *J. Porous Mater.* 24 (3), 613–620.
- Gao, G., Lu, S., Dong, B., Xiang, Y., Xi, K., Ding, S., 2016b. Mesoporous Co3V2O8 nanoparticles grown on reduced graphene oxide as a high-rate and long-life anode material for lithium-ion batteries. *J. Mater. Chem. A* 4 (17), 6264–6270.
- Gao, S., et al., 2016a. Formation of Sn–M (M=Fe Al Ni) alloy nanoparticles by DC arc-discharge and their electrochemical properties as anodes for Li-ion batteries. *J. Solid State Chem.* 242, 127–135.
- Gao, S., et al., 2017. Nanostructured Sn–M (M = Cu Mg and Fe) intermetallic alloys and their electrochemical activity as anode electrodes in a Li-ion battery. *J. Alloys Compd.* 706, 401–408.
- Goodenough, J.B., Park, K.S., 2013. The Li-ion rechargeable battery: A perspective. *J. Am. Chem. Soc.* 135 (4), 1167–1176.
- Goriparti, S., Miele, E., De Angelis, F., Di Fabrizio, E., Proietti Zaccaria, R., Capiglia, C., 2014. Review on recent progress of nanostructured anode materials for Li-ion batteries. *J. Power Sources* 257, 421–443.
- Guan, D., Li, J., Gao, X., Yuan, C., 2014. A comparative study of enhanced electrochemical stability of tin-nickel alloy anode for high-performance lithium ion battery. *J. Alloys Compd.* 617, 464–471.
- Guo, Y., et al., 2020. Core–shell ZnO@C:N hybrids derived from MOFs as long-cycling anodes for lithium ion batteries. *Chem. Commun.* 56 (13), 1980–1983.
- Hai Tian, B.Z., Wu, Zhenguo, Zhong, Yanjun, Yang, Xiushan, Guo, Xiaodong, Wang, Xinlong, 2020. Rapid in-situ fabrication of Fe3O4_Fe7S8@C composite as anode materials for lithium-ion batteries _Elsevier Enhanced Reader.pdf. *Mater. Res. Bull.* 133 (2021), 111021.
- He, M., Walter, M., Kravchyk, K.V., Erni, R., Widmer, R., Kovalenko, M.V., 2015. Monodisperse SnSb nanocrystals for Li-ion and Na-ion battery anodes: Synergy and dissonance between sn and sb. *Nanoscale* 7 (2), 455–459.
- He, Y., Xu, L., Li, C., Chen, X., Xu, G., Jiao, X., 2018. Mesoporous Mn–Sn bimetallic oxide nanocubes as long cycle life anodes for Li-ion half/full cells and sulfur hosts for Li-S batteries. *Nano Res.* 11 (7), 3555–3566.
- Huang, Q., et al., 2016. Hollow carbon nanospheres with extremely small size as anode material in lithium-ion batteries with outstanding cycling stability. *J. Phys. Chem. C* 120 (6), 3139–3144.
- Huang, G., et al., 2020. Ultrastable silicon anode by three-dimensional nanoarchitecture design. *ACS Nano*.
- Huy, V.P.H., So, S., Kim, I.T., Hur, J., 2021. Self-healing gallium phosphide embedded in a hybrid matrix for high-performance Li-ion batteries. *Energy Storage Mater.* 34, 669–681.
- Hwang, H., Kim, H., Cho, J., 2011. MoS₂ Nanoplates consisting of disordered graphene-like layers for high rate lithium battery anode materials. *Nano Lett.* 11 (11), 4826–4830.
- Imanishi, N., Takeda, Y., Yamamoto, O., 2007. Development of the carbon anode in lithium ion batteries. *Lithium Ion Batter.* 98–126.
- Ivanova, N., 2017. The electrochemistry of intermetallic compounds: A mini-review. *Electrochim. commun.* 80 (May), 48–54.
- Jia, C., Zhang, X., Yang, P., 2018. Anatase/rutile-TiO₂ hollow hierarchical architecture modified by SnO₂ toward efficient lithium storage. *Int. J. Hydrogen Energy* 3, 2237–2246.
- Jiang, J., et al., 2019a. Auto-adjustment of structure and SnO₂ content of SnO₂/TiO₂ microspheres for lithium-ion batteries. *Chem. Eng. J.* 359 (November 2018), 746–754.
- Jiang, J., et al., 2019b. Auto-adjustment of structure and SnO₂ content of SnO₂/TiO₂ microspheres for lithium-ion batteries. *Chem. Eng. J.* 359 (October 2018), 746–754.
- Jiao, S., et al., 2018. Sn-Doped rutile TiO₂ hollow nanocrystals with enhanced lithium-ion batteries performance. *ACS Omega* 3 (1), 1329–1337.
- Kasinathan, K., Kennedy, J., Elayaperumal, M., Henini, M., Malik, M., 2016. Photodegradation of organic pollutants RhB dye using UV simulated sunlight on ceria based TiO₂ nanomaterials for antibacterial applications. *Sci. Rep.* 6 (September), 1–12.
- Kepler, K.D., Vaughney, J.T., Thackeray, M.M., 1999. Copper-tin anodes for rechargeable lithium batteries: An example of the matrix effect in an intermetallic system. *J. Power Sources* 81–82, 383–387.
- Kim, H., Kim, M.G., Shin, T.J., Shin, H.J., Cho, J., 2008. TiO₂@Sn core–shell nanotubes for fast and high density Li-ion storage material. *Electrochim. commun.* 10 (11), 1669–1672.

- Kim, H.J., et al., 2020. A comprehensive review of li-ion battery materials and their recycling techniques. 9, (7).
- Kulova, T.L., 2013. New electrode materials for lithium-ion batteries (review). Russ. J. Electrochem. 49 (1), 1–25.
- Kumar, R., et al., 2020. Heteroatom doped graphene engineering for energy storage and conversion. Mater. Today 39 (xx), 47–65.
- Kwon, H.J., et al., 2020. Nano/microstructured silicon-carbon hybrid composite particles fabricated with corn starch biowaste as anode materials for li-ion batteries. Nano Lett. 20 (1), 625–635.
- Lee, D.H., Park, J.G., Kyoung, J.C., Choi, H.J., Kim, D.W., 2008. Preparation of brookite-type TiO₂/carbon nanocomposite electrodes for application to Li ion batteries. Eur. J. Inorg. Chem. (6), 878–882.
- Lee, G.H., Shim, H.W., Kim, D.W., 2015. Superior long-life and high-rate Ge nanoarrays anchored on Cu/C nanowire frameworks for Li-ion battery electrodes. Nano Energy 13, 218–225.
- Li, L., Seng, K.H., Feng, C., Liu, H.K., Guo, Z., 2013. Synthesis of hollow GeO₂ nanostructures, transformation into Ge@C, and lithium storage properties. J. Mater. Chem. A 1 (26), 7666–7672.
- Li, R., Xiao, W., Miao, C., Fang, R., Wang, Z., Zhang, M., 2019. Sphere-like SnO₂/TiO₂ composites as high-performance anodes for lithium ion batteries. Ceram. Int. 45 (10), 13530–13535.
- Li, X., Zhang, Y., Li, T., Zhong, Q., Li, H., Huang, J., 2014. Carbon encapsulated ultrasmall SnO₂ nanoparticles anchoring on graphene/TiO₂ nanoscrolls for lithium storage. Electrochim. Acta 147, 40–46.
- Li, X., Zhang, X., Wang, R., Su, Z., Sha, J., Liu, P., 2016a. Graphene nanoribbons wrapping double nanoshells of SnO₂@TiO₂ for high lithium storage. J. Power Sources 336, 298–306.
- Li, M., Zhou, D., Song, W.L., Li, X., Fan, L.Z., 2015. Highly stable GeOx@C core-shell fibrous anodes for improved capacity in lithium-ion batteries. J. Mater. Chem. A 3 (39), 19907–19912.
- Li, X.Y., et al., 2016b. Inserting Sn nanoparticles into the pores of TiO₂-x-C nanofibers by lithiation. Adv. Funct. Mater. 26 (3), 376–383.
- Li, X., et al., 2018a. Self-organized TiO₂ network decorated with SnO₂ nanoparticles as an anode for lithium-ion batteries. J. Alloys Compd. 752, 68–75.
- Li, X., et al., 2018b. Self-organized TiO₂ network decorated with SnO₂ nanoparticles as an anode for lithium-ion batteries. J. Alloys Compd. 752, 68–75.
- Li, J., et al., 2020. MXene-decorated SnS₂/Sn₃S₄ hybrid as anode material for high-rate lithium-ion batteries. Chem. Eng. J. 380 (August 2019), 122590.
- Liao, J.Y., Higgins, D., Lui, G., Chabot, V., Xiao, X., Chen, Z., 2013. Multifunctional TiO₂-C/MnO₂ core-double-shell nanowire arrays as high-performance 3D electrodes for lithium ion batteries. Nano Lett. 13 (11), 5467–5473.
- Liu, M., Yan, C., Zhang, Y., 2015. Fabrication of Nb205 nanosheets for high-rate lithium ion storage applications. Sci. Rep. 5, 8326.
- Liu, Q., Ye, J., Chen, Z., Hao, Q., Xu, C., Hou, J., 2019a. Double conductivity-improved porous Sn/Sn 4 3 @carbon nanocomposite as high performance anode in lithium-ion batteries. J. Colloid Interface Sci. 537, 588–596.
- Liu, Z., et al., 2019b. Three-dimensional ordered porous electrode materials for electrochemical energy storage. NPG Asia Mater. 11 (1).
- Liu, Q., et al., 2020. 3D Branched rutile TiO₂ @ rutile sno₂ nanorods array heteroarchitectures/carbon cloth with an adjustable band gap to enhance lithium storage reaction kinetics for flexible lithium-ion batteries. Electrochim. Acta 354, 136727.
- Lü, X., Xia, B., Liu, C., Yang, Y., Tang, H., 2016. TiO₂-Based nanomaterials for advanced environmental and energy-related applications. J. Nanomat. 2016.
- Lübke, M., et al., 2015. High power TiO₂ and high capacity Sn-doped TiO₂ nanomaterial anodes for lithium-ion batteries. J. Power Sources 294, 94–102.
- Luo, J., et al., 2013. Rationally designed hierarchical TiO₂@Fe₂O₃ hollow nanostructures for improved lithium ion storage. Adv. Energy Mater. 3 (6), 737–743.
- Luo, G., et al., 2015. Hierarchical mesoporous SnO₂@C@TiO₂ nanochains for anode material of lithium-ion batteries with excellent cycling stability. Electrochim. Acta 184, 219–225.
- Lyu, Y., et al., 2021. An overview on the advances of LiCoO₂ cathodes for lithium-ion batteries. Adv. Energy Mater. 11 (2), 1–29.
- Ma, X., Zhou, Y., Chen, M., Wu, L., 2017. Synthesis of olive-like nitrogen-doped carbon with embedded Ge nanoparticles for ultrahigh stable lithium battery anodes. Small 13 (20), 1–8.
- Ma, T., et al., 2019. N-doped carbon-coated tin sulfide/graphene nanocomposite for enhanced lithium storage. Electrochim. Acta 300, 131–137.
- Mao, M., et al., 2017. Pipe-wire TiO₂-Sn@Carbon nanofibers paper anodes for lithium and sodium ion batteries. Nano Lett. 17 (6), 3830–3836.
- Mohamed, E.F., 2017. Nanotechnology: Future of environmental air pollution control. Environ. Manag. Sustain. Dev. 6 (2), 429.
- Nanko, M., 2009. Definitions and categories of hybrid materials. Adv. Tech. Mat. Mat. Proc. J. 6 (January 2009), 1–8.
- Nie, S., et al., 2018. Nitrogen-doped TiO₂-C composite nanofibers with high-capacity and long-cycle life as anode materials for sodium-ion batteries. Nano-Micro Lett. 10 (4), 1–13.
- (P & S) Intelligence, 2019. Global Market Size, Share, Development, Growth, and Demand Forecast. 2013–2023, pp. 1–5.
- Park, C.M., Chang, W.S., Jung, H., Kim, J.H., Sohn, H.J., 2009. Nanostructured Sn/TiO₂/C composite as a high-performance anode for Li-ion batteries. Electrochim. Commun. 11 (11), 2165–2168.
- Peng, Z., Shi, Z., Liu, M., 2000. Mesoporous Sn-TiO₂ composite electrodes for lithium batteries. Chem. Commun. 3 (21), 2125–2126.
- Povolotskaya, A.V., et al., 2015. Hybrid nanostructures: synthesis, morphology and functional properties. Russ. Chem. Rev. 84 (6), 579.
- Sakaguchi, H., Honda, H., Akasaka, Y., Esaka, T., 2003. Ce-Sn intermetallic compounds as new anode materials for rechargeable lithium batteries. J. Power Sources, 119–121, 50–55.
- Shi, X., et al., 2017. SnO₂/TiO₂ Nanocomposites embedded in porous carbon as a superior anode material for lithium-ion batteries. Chem. Eng. J. 330 (July), 453–461.
- Shukla, A.K., Prem Kumar, T., 2013. Nanostructured electrode materials for electrochemical energy storage and conversion. Wiley Interdiscip. Rev. Energy Environ. 2 (1), 14–30.
- Simon, P., Gogotsi, Y., Dunn, B., 2014. Where do batteries end and supercapacitors begin? Science (80–) 343 (March), 1210–1211.
- Su, L., Jing, Y., Zhou, Z., 2011. Li ion battery materials with core-shell nanostructures. Nanoscale 3 (10), 3967–3983.
- Sun, Y., Liu, N., Cui, Y., 2016. Promises and challenges of nanomaterials for lithium-based rechargeable batteries. Nat. Energy 1 (7).
- Sun, L., et al., 2019. Sn-SnO₂ hybrid nanoclusters embedded in carbon nanotubes with enhanced electrochemical performance for advanced lithium ion batteries. J. Power Sources 415 (September 2018), 126–135.
- Sun, H., et al., 2021. Facile synthesis of hetero-structured few-layer MoS₂-coated MoO₂ as superior anode materials of lithium ion batteries. J. Alloys Compd. 851.
- Tasdemir, A., Bulut Kopuklu, B., Kirlioglu, A.C., Alkan Gursel, S., Yurum, A., 2021. The influence of nitrogen doping on reduced graphene oxide as highly cyclable Li-ion battery anode with enhanced performance. Int. J. Hydrog. Energy.
- Taylor, M.P., Chen, J.J.J., 2015. Technique for low amperage potline operation for electricity grid storage. Metall. Mater. Trans. E 2 (1), 87–98.
- Tian, Q., Chen, Y., Zhang, F., Zhang, W., Sui, Z., Yang, L., 2020. Hierarchical carbon-riveted 2D@0D TiO₂ nanosheets@SnO₂ nanoparticles composite for a improved lithium-ion battery anode. Appl. Surf. Sci. 511 (October 2019), 145625.
- Tian, Q., Li, L., Chen, J., Yang, L., ichi Hirano, S., 2018a. Facile fabrication of robust TiO₂@SnO₂@C hollow nanobelts for outstanding lithium storage. J. Power Sources 376 (August 2017), 1–10.
- Tian, Q., Li, L., Yang, L., Chen, J., ichi Hirano, S., 2018b. A robust strategy for stabilizing SnO₂: TiO₂-supported and carbon-immobilized TiO₂/SnO₂/C composite towards improved lithium storage. Electrochim. Acta 259, 815–821.
- Tian, Q., Mao, Y., Zhang, X., Yang, L., 2018c. Heterogeneous nanocrystals assembled TiO₂ /SnO₂ /C composite for improved lithium storage. Appl. Surf. Sci. 447, 408–415.
- Tian, Q., Tian, Y., Zhang, W., Huang, J., Zhang, Z., Yang, L., 2017a. Impressive lithium storage of SnO₂@TiO₂ nanospheres with a yolk-like core derived from self-assembled sno₂nanoparticles. J. Alloys Compd. 702, 99–105.
- Tian, Q., Xu, H., Li, L., Bao, D., 2017b. Fabrication of novel hetero-nanostructure of SnO₂@TiO₂@C for improved lithium storage. Mater. Lett. 209, 197–200.
- Tian, Q., Yan, J., Yang, L., Chen, J., 2018d. Fabrication of three-dimensional carbon coating for SnO₂/TiO₂ hybrid anode material of lithium-ion batteries. Electrochim. Acta 282, 38–47.
- Tran, T., McCormac, K., Li, J., Bi, Z., Wu, J., 2014. Electrospun sno₂ and TiO₂ composite nanofibers for lithium ion batteries. Electrochim. Acta 117, 68–75.
- Trifonova, A., Wachtler, M., Winter, M., Besenhard, J.O., 2002. Sn-Sb and Sn-Bi alloys as anode materials for lithium-ion batteries. Ionics (Kiel) 8 (5–6), 321–328.
- Wan, Lijuan, Ren, Zhaoyu, Wang, Hui, Wang, Gang, Tong, Xin, Gao, Shuanghong, Bai, Jintao, 2011. Graphene nanosheets based on controlled exfoliation process for enhanced lithium storage in lithium-ion battery. Diam. Relat. Mater. 20 (5–6), 756–761.
- Wan, L., et al., 2021. In-situ construction of g-C3N4/Mo2CTx hybrid for superior lithium storage with significantly improved Coulombic efficiency and cycling stability. Chem. Eng. J. 410 (October 2020), 128349.
- Wang, B., Bai, Y., Xing, Z., Hulicova-Jurcakova, D., Wang, L., 2015. Enhanced performance of a pillared TiO₂ nanohybrid as an anode material for fast and reversible lithium storage. ChemNanoMat 1 (2), 96–101.
- Wang, X.L., Han, W.Q., Chen, J., Graetz, J., 2010a. Single-crystal intermetallic M-Sn (M = Fe, Cu, Co, Ni) nanospheres as negative electrodes for lithium-ion batteries. ACS Appl. Mater. Interfaces 2 (5), 1548–1551.
- Wang, Y., Li, H., He, P., Hosono, E., Zhou, H., 2010b. Nano active materials for lithium-ion batteries. Nanoscale 2 (8), 1294–1305.
- Wang, G., Lu, Z.W., Gao, X.P., Liu, X.J., Wang, J.Q., 2009. Electrochemical performance of La-Co-Sn alloys as anode materials for Li-ion batteries. J. Power Sources 189 (1), 655–659.

- Wang, B., Luo, B., Li, X., Zhi, L., 2012a. The dimensionality of Sn anodes in Li-ion batteries. *Mater. Today* 15 (12), 544–552.
- Wang, H., Ma, D., Huang, X., Huang, Y., Zhang, X., 2012b. General and controllable synthesis strategy of metal oxide/TiO₂ hierarchical heterostructures with improved lithium-ion battery performance. *Sci. Rep.* 2, 1–8.
- Wang, Y., Xu, M., Peng, Z., Zheng, G., 2013a. Direct growth of mesoporous Sn-doped TiO₂ thin films on conducting substrates for lithium-ion battery anodes. *J. Mater. Chem. A* 1 (42), 13222–13226.
- Wang, X., Zhao, Y., Mølhav, K., Sun, H., 2017. Engineering the surface/interface structures of titanium dioxide micro and nano architectures towards environmental and electrochemical applications. *Nanomaterials* 7 (11).
- Wang, B., et al., 2013b. Adaptable silicon-carbon nanocables sandwiched between reduced graphene oxide sheets as lithium ion battery anodes. *ACS Nano* 7 (2), 1437–1445.
- Wang, X., et al., 2013c. TiO₂ modified FeS nanostructures with enhanced electrochemical performance for lithium-ion batteries. *Sci. Rep.* 3, 1–8.
- Wang, S., et al., 2020a. Encapsulation of SnO₂ nanoparticles between the hollow TiO₂ nanosphere and the carbon layer as high-performance negative materials for lithium-ion batteries. *J. Alloys Compd.* 814, 152342.
- Wang, X., et al., 2020b. In situ incorporation of super-small metallic high capacity nanoparticles and mesoporous structures for high-performance TiO₂/SnO₂/Sn/Carbon nanohybrid lithium-ion battery anodes. *Energy Technol.* 8 (6), 2–11.
- Wei, W., Guo, L., 2013. One-step in situ synthesis of GeO₂/graphene composites anode for high-performance li-ion batteries. Part. Part. Syst. Charact. 30 (8), 658–661.
- Wei, Z., Mao, H., Huang, T., Yu, A., 2013. Facile synthesis of Sn/TiO₂ nanowire array composites as superior lithium-ion battery anodes. *J. Power Sources* 223, 50–55.
- Xiao, L., et al., 2012. High capacity reversible alloying reactions in SnSb/C nanocomposites for Na-ion battery applications. *Chem. Commun.* 48 (27), 3321–3323.
- Xie, K., Wei, B., 2014. Materials and structures for stretchable energy storage and conversion devices. *Adv. Mater.* 26 (22), 3592–3617.
- Xin, W., Gao, T., Zhang, W., Hu, T., Sun, X., Zhou, G., 2019. Three-dimensional hollow SnO₂@TiO₂ spheres encapsulated in reduced graphene oxide aerogels as promising anodes for lithium-ion storage. *J. Alloys Compd.* 784, 157–164.
- Xin, F., et al., 2015. A lithiation/delithiation mechanism of monodispersed MSn₅ (M = Fe, Co and FeCo) nanospheres. *J. Mater. Chem. A* 3 (13), 7170–7178.
- Xu, G.L., et al., 2012. Facile synthesis of porous MnO/C nanotubes as a high capacity anode material for lithium ion batteries. *Chem. Commun.* 48 (68), 8502–8504.
- Yang, S., Huang, Y., Han, G., Liu, J., Cao, Y., 2017a. Synthesis and electrochemical performance of double shell SnO₂@amorphous TiO₂ spheres for lithium ion battery application. *Powder Technol.* 322, 84–91.
- Yang, S., Huang, Y., Han, G., Liu, J., Cao, Y., 2017b. Synthesis and electrochemical performance of double shell SnO₂@amorphous TiO₂ spheres for lithium ion battery application. *Powder Technol.* 322, 84–91.
- Yang, C., Zhang, D., Zhao, Y., Lu, Y., Wang, L., Goodenough, J.B., 2011. Nickel foam supported Sn-Co alloy film as anode for lithium ion batteries. *J. Power Sources* 196 (24), 10673–10678.
- Yi, T.F., Qu, J.P., Lai, X., Han, X., Chang, H., Zhu, Y.R., 2021. Toward high-performance Li storage anodes: design and construction of spherical carbon-coated CoNiO₂ materials. *Mater. Today Chem.* 19.
- Yi, Z., et al., 2016. Facile fabrication of SnO₂@TiO₂ core-shell structures as anode materials for lithium-ion batteries. *J. Mater. Chem. A* 4, 12850–12857.
- Yin, J., Wada, M., Yoshida, S., Ishihara, K., Tanase, S., Sakai, T., 2003. New Ag-Sn alloy anode materials for lithium-ion batteries. *J. Electrochem. Soc.* 150 (8), A1129.
- Yin, H., et al., 2017. Hollow porous CuO/C composite microcubes derived from metal-organic framework templates for highly reversible lithium-ion batteries. *J. Alloys Compd.* 706, 97–102.
- Yu, C., Bai, Y., Yan, D., Li, X., Zhang, W., 2014. Improved electrochemical properties of Sn-doped TiO₂ nanotube as an anode material for lithium ion battery. *J. Solid State Electrochem.* 18 (7), 1933–1940.
- Zeng, T., Ji, P., Hu, X., Li, G., 2016. Nano-Sn doped carbon-coated rutile TiO₂ spheres as a high capacity anode for Li-ion battery. *RSC Adv.* 6 (54), 48530–48536.
- Zhang, Y., Tang, Y., Li, W., Chen, X., 2016a. Nanostructured TiO₂-based anode materials for high-performance rechargeable lithium-ion batteries. *ChemNanoMat* 2 (8), 764–775.
- Zhang, C.Q., Tu, J.P., Huang, X.H., Yuan, Y.F., Wang, S.F., Mao, F., 2008. Preparation and electrochemical performances of nanoscale FeSn₂ as anode material for lithium ion batteries. *J. Alloys Compd.* 457 (1–2), 81–85.
- Zhang, P., et al., 2016b. Photochemical synthesis of SnO₂/TiO₂composite nanotube arrays with enhanced lithium storage performance. *J. Alloys Compd.* 674, 1–8.
- Zhao, F., et al., 2017. Directly grown carbon nanotube based hybrid electrodes with enhanced thermo-cell performances. *RSC Adv.* 7 (38), 23890–23895.
- Zhao, X., et al., 2020. High-performance Li-ion batteries based on graphene quantum dot wrapped carbon nanotube hybrid anodes. *Nano Res.* 13 (4), 1044–1052.
- Zhou, Y., Jo, C., Lee, J., Lee, C.W., Qao, G., Yoon, S., 2012. Development of novel mesoporous C-TiO₂-SnO₂ nanocomposites and their application to anode materials in lithium ion secondary batteries. *Microporous Mesoporous Mater.* 151, 172–179.
- Zhu, S., Lin, Y., Yan, Z., Jiang, J., Yang, D., Du, N., 2021. Novel design of uniform Si@graphite@C composite as high-performance Li-ion battery anodes. *Electrochim. Acta* 377, 138092.
- Zhu, H., et al., 2013. Tin anode for sodium-ion batteries using natural wood fiber as a mechanical buffer and electrolyte reservoir. *Nano Lett.* 13 (7), 3093–3100.