

Review on Recent Progress of Nanostructured Anode Materials for Li-Ion Batteries

Thevabakthi Siluvai Muthu Arul Jeevan^{1*}, Gashaw Tadele¹, Liyew Yizengaw¹,
Maria Francis George Johnson²

¹Department of Chemistry, College of Natural and Computational Sciences, Mizan Tepi University, Mizan Teferi, Ethiopia

²Department of Chemistry, Loyola College, Chennai, India

Email: *arul@mtu.edu.et

How to cite this paper: Jeevan, T.S.M.A., Tadele, G., Yizengaw, L. and Johnson, M.F.G. (2022) Review on Recent Progress of Nanostructured Anode Materials for Li-Ion Batteries. *American Journal of Analytical Chemistry*, 13, 431-448.
<https://doi.org/10.4236/ajac.2022.1311029>

Received: October 25, 2022

Accepted: November 8, 2022

Published: November 11, 2022

Copyright © 2022 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Lithium ion battery (LIB) is one of the promising power storage devices in today's world. Lithium ion battery like other types of electrochemical cell has anodic and cathodic electrode in which lithium ion is intercalated and deintercalated during charging and discharging process respectively. The capacity of lithium ion battery is improved by the development of innovative kinds of electrode. Carbon, metal/semiconductor, metal oxides and metal phosphides/nitrides/sulfides based nanomaterials improve the capability of LIBs due to their high surface area, low diffusion distance, high electrical and ionic conductivity. Nanostructured materials represent a rapidly growing area in the field of Li-ion batteries because of their substantial advantages in terms of mass transport. In this review anode nanomaterials classified based on type of transition metal/semiconductor such as carbon, silicon, titanium and tin based nanomaterials are discussed. Additionally, different electrochemical reactions, comparative influence of anode materials on LIBs and their applications are widely explained.

Keywords

Lithium Ion Battery, Semiconductor, Nanostructure, Composite Materials, Ti Based Materials

1. Introduction

Li-ion batteries have high energy and power density, which makes it the technology of choice for portable electronics, power tools, and hybrid/full electric vehicles. Also reduce green house effect (CO₂ emissions) by replacing many gasoline-powered transportations. Due to depletion of non-renewable fossil fuels and its environmental issues, lithium ion battery is preferred as source of world

energy source. Electrical energy storage, such as batteries has the ability to highly store electricity in chemicals and release it according to demand. Among rechargeable battery lithium ion battery currently offers high energy and power density. However, lithium ion battery also still unable to provide energy for electronic materials which need high energy density, such as plug-in hybrid electric vehicles (PHEV) and all electric vehicles (EV). Therefore it requires significant improvements in many perspectives, such as energy density, safety, durability and cost [1]. The comparatively high energy density of Li^+ batteries make it to have many uses, in electric grid transportations, improving the quality of energy harvested from wind, solar, geo-thermal and other renewable sources, thus contributing to their more widespread use and building an energy-sustainable economy [2].

Lithium has lightest density (0.53 g/cm^3) and it is most electropositive (-3.04 V vs hydrogen electrode), these unique properties make Li preferable anode materials in batteries. These exciting properties also result in high voltage, energy and power density in the battery. Early in 1970 lithium can be used as anode materials in lithium battery (primary battery), and offered high voltage. However, dendritic growth of Li metal, leads to shorting of electrodes and thermal runaway, and this problem leads to the development of new anode for lithium ion. Instead to improve these effects Li metal was substituted by a Li insertion compound, rather than acting as anode. Most lithium ion batteries use graphite anode because it offers a high cell voltage in the range of $3.0 - 3.7 \text{ V}$, when compared with Ni-Cd and Ni-MH batteries which show much lower voltage ($1.2 - 1.5 \text{ V}$) [1].

A source of Li^+ in Li-ion battery is a positive electrode (cathode). In addition lithium ion battery has non aqueous liquid electrolyte, polymeric separator, and negative electrode (anode) which can accept Li ions. The well known cathode and anode used in lithium ion battery are layered LiCoO_2 and graphite, respectively. Organic liquid containing lithium salt such as, 1M LiPF_6 dissolved in a mixture of ethylene carbonate-diethylene carbonate (EC-DEC) or ethylene carbonate-dimethyl carbonate (EC-DMC) used as electrolyte [3]. There are many effective materials which used as cathodes in lithium ion batteries such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 . Generally, their high conductive resistance easily results in a serious polarization and poor utilization of active anode materials [4].

There are different types of Li-ion batteries based on different anode materials, cathode materials, electrolytes and separators. A very simplified view of the most commonly used cell materials is presented in **Figure 1** [5]. Both electrodes allow lithium ions to move in and out of their interiors. During charging lithium ion moves toward anode (intercalation), while discharging the lithium ion moves toward cathode. The charge/discharge processes are shown in the following sketches [6].

The following equations show the general chemistry that occurs at anode and cathode in lithium ion batteries while charging:

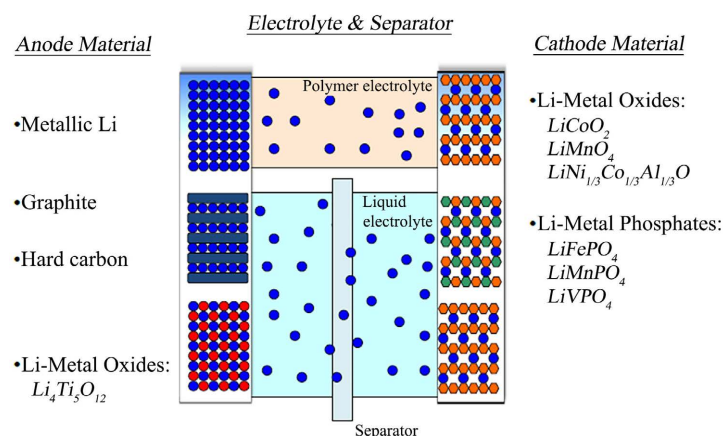
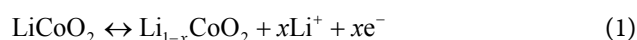
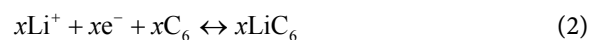


Figure 1. Overview of the most commonly commercialised Li-ion battery concepts.

The cathode half-reaction:



The anode half reaction:



In addition to graphite, there are many alternative materials used as anodes in lithium ion batteries, such as carbon based materials (CNT, graphene and porous carbon), metal (Sn, In, etc.), metalloids (Si, Sb and Ge, etc.) and transition metal oxides (Fe, Mn, Ni, Cu and Co) [7].

2. Nanostructured Material for Rapidly Growing Lithium Ion Battery Technology

Now a day's nanostructured materials are widely used in the field of Li-ion batteries because of their great advantages in terms of mass transport, higher electrode-electrolyte contact area, and better movement of lithium ion during intercalation and deintercalation. Generally, nanocomposites show higher reversible capacity and better cycling behavior than their large structural materials. In addition, nanocomposites have large surface/volume ratio and the geometry which make it efficient electrode materials for powerful electrochemical energy storage devices with both high energy and power density. C, Si, TiO_2 and SnO_2 based nanomaterials have received a great attention, and considered as alternative anode materials for lithium ion batteries [8].

Graphite anodes have a theoretical lithium storage capacity of 372 mAh/g to form LiC_6 intercalation compound. Recently, many efforts in research are currently made to increase this limited capacity. Nanostructured anodes can be used to increase this limited capacity due to three reasons:

1) Decreasing the size of the active particles to the nano range; result in larger surface/volume ratio which implies a larger specific capacity and contact area with the electrolyte leading to high lithium ion movement across the electrode/

electrolyte interface [9].

2) The reduction of the size of the particles result in decreasing the path length for lithium ion implies a reduction of the length of the electron and Li^+ inside the particles. Therefore the conductivity is going to be increased, because after the electron has reached the surface of a particle it is driven to the current collector in a conductive medium immediately [10].

3) The intercalation of lithium ion is accompanied with a dilatation of the particles, which may result in the formation of cracks, or even pulverization when the particle size is in the micron range [9] [10].

During Charging/discharging process in Li-ion batteries mainly three types of reactions occurs:

- Diffusion of Li^+ and electron within solid electrode materials (anode and cathode).
- Charge transfer at electrode electrolyte interface.
- Movement of Li^+ ion in the electrolyte.

Diffusion of Li ions across Solid state is known as the rate-controlling step for Li-ion batteries which determine the rate of charge/discharge. The time for Li ion diffusion can be expressed as a function of diffusion coefficient of Li ions and the diffusion length as following:

$$\tau = \frac{L^2_{\text{ion}}}{D_{\text{Li}}}$$

where L ion is the diffusion length of solid materials and D_{Li} is the diffusion coefficient of Li ions. As shown from Equation that a faster diffusion can be achieved in a system with higher diffusion coefficient and lower diffusion length. Diffusion coefficient of Li ions in most electrode materials is very low (10^{-7} - 10^{-11} cm^2/s) and has large diffusion length, which result in more diffusion time. Nanostructured materials are capable to improve rate performance of Li ion batteries because of its low diffusion length and high diffusion coefficient [11]. Here the authors compared the data with different anode materials and are listed in **Table 1**.

Table 1. Comparison of the theoretical specific capacity, charge density, volume change and potential of various anode materials.

Materials	Li	C	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	Si	Sn	Sb	Al	Mg	Bi
Density ($\text{g}\cdot\text{cm}^{-3}$)	0.53	2.25	3.5	2.33	7.29	6.7	2.7	1.3	9.78
Lithiated phase	Li	LiC_6	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	$\text{Li}_{4.4}\text{Si}$	$\text{Li}_{4.4}\text{Sn}$	Li_3Sb	LiAl	Li_3Mg	Li_3Bi
Theoretical specific capacity ($\text{mAh}\cdot\text{g}^{-1}$)	3862	372	175	4200	994	660	993	3350	385
Theoretical charge density ($\text{mAh}\cdot\text{cm}^{-3}$)	2047	837	613	9786	7246	4422	2681	4355	3765
Volume change (%)	100	12	1	320	260	200	96	100	215
Potential vs. Li (~V)	0	0.05	1.6	0.4	0.6	0.9	0.3	0.1	0.8

3. Classification of Anode Nanomaterials

Different materials can be used as anode in lithium ion batteries, which have different capacity. The large size of nanomaterials offers low capacity as compared to its nanostructure. In order to address this large capacity nanomaterials different semiconductor, metals and metalloids can be synthesized currently. Some of nanomaterials that used most commonly in lithium ion batteries can be discussed in this review.

3.1. Carbon Based Nanomaterials Anode for Lithium Ion Battery

3.1.1. Porous Carbon

Porous carbon materials, such as microporous (pore size < 2 nm), mesoporous (2 nm < pore size < 50 nm), macroporous (pore size > 50 nm) materials, can provide extra capacities for lithium ion batteries, which are much higher than that of graphite. Porous structures, offer large surface area and providing more active positions to combine Li-ions, which provide extra capacities for lithium ion batteries. Many researchers have demonstrated that micro/mesopores can store large amounts of Li-ions. Therefore, porous carbon materials often result in enhanced capacities and good cycling performances, owing to large surface areas and small mechanical stresses of volume expansion/contraction during cycling [7].

3.1.2. Carbon Nanotubes (CNTs)

Carbon nanotubes consist of carbon atoms that are structured in layers of graphene into the shape of a cylinder. One carbon atom of a graphene is symmetrically bound to the other three carbon atom [12].

Carbon nanotubes (CNTs) are one dimensional nanomaterial and classified in to:

- Single-walled carbon nanotube (SWCNT) rolled up by one-layer graphene.
- Multiwalled carbon nanotube (MWCNT) rolled up by multilayer graphene.

CNTs have light weight and perfect connection in their hexagonal structure which offers it excellent mechanical, electrical and chemical properties. Currently, CNTs has many emerging application due to its excellent electrochemical properties, low density, high rigidity, and high tensile strength. CNTs are widely used in lithium-ion batteries, both as the anode material and the conductive additive in the composite electrodes [13].

Single wall carbon nanotubes (SWCNTs) are promising nanomaterials which have reversible capacity $1116 \text{ mAh}\cdot\text{g}^{-1}$. A purified single-wall carbon nanotube (SWCNT) delivered a capacity larger than $1050 \text{ mAh}\cdot\text{g}^{-1}$ [3]. Multi-wall carbon nanotubes (MWCNT) which have high capacity can be formed introducing 10 nm thick layer of Al_2O_3 by atomic layer deposition (ALD) on to electrodes. The resultant MWCNT anode has a stable capacity of $1100 \text{ mAh}\cdot\text{g}^{-1}$ in 50 charge-discharge cycles at the current rate of $372 \text{ mA}\cdot\text{g}^{-1}$. Al_2O_3 adsorbed to EC (Ethylene Carbonate) molecules of the electrolyte decreases the decomposition of the

electrolyte. However, the results are obtained at the laboratory scale and different from result gained with commercial products. Commercial MWCNTs have a typical capacity close to $250 \text{ mAh}\cdot\text{g}^{-1}$, and after purification, the capacity rise to $400 \text{ mAh}\cdot\text{g}^{-1}$. Li insertion induce large stresses during cycling in lithium ion batteries because MWCNTs close structure does not allow expansion of graphene sheets as in graphite, therefore MWCNTs show a tendency to suffer from Li-induced embrittlement. In contrast the promising results reported, the carbon nanotubes have not found a place in the industry of the lithium-ion batteries, because of their cost and the difficulty to prepare them free of any large structural defects and high voltage hysteresis [14].

3.1.3. Graphene

Graphene is a monolayer of graphite, which contain sp^2 hybridized carbon atoms arranged in a honeycomb crystal lattice. Graphene forms the basic structure for other carbon materials like graphite, carbon nanotubes and fullerenes. Also, it is two-dimensional carbon material with a specific surface area of $2600 \text{ m}^2/\text{G}$ resulting in higher lithium storage capacity. Furthermore, its high electron mobility ($15,000 \text{ cm}^2/(\text{V}\cdot\text{s})$), outstanding thermal conductivity ($3000 \text{ W}/(\text{m}\cdot\text{K})$), good chemical stability and excellent mechanical properties make unique for forming composite materials used as negative electrode. Composite electrodes also allow for the storage of more lithium ions and increase the battery's capacity. As a result, the life of batteries containing graphene can last significantly longer than conventional batteries [1].

In conventional lithium ion batteries, no storing of lithium ions (lithium ions are inserted and removed immediately) in the electrode materials, as a result the materials will swell and shrink, leading to a quicker breakdown. This can be avoided through the addition of graphene, which has efficient conductivity and less heat resistant within the electrode, so batteries can operate at lower temperatures, which ultimately improves the battery's safety. Graphene has many additional characteristics such as the quantum hall effect, bipolar field-effect, ferromagnetism, superconductivity and high electron mobility. These properties make graphene suited for use in many fields [15].

The introduction of heteroatoms such as nitrogen in to graphene can further enhance its electrochemical performance. Nitrogen is more electronegative than carbon but has a similar atomic diameter, which lead to enhanced interaction between a nitrogen-doped carbon material and lithium ions. In addition the presence of nitrogen introduces more defects, providing more active sites for lithium storage [16] [17]. Graphene is building blocks for carbonaceous materials of other dimensionalities (that is, graphite, fullerenes and carbon nanotubes) and listed in **Table 2**.

3.1.4. Hard Carbon Nanomaterial for Lithium Ion Batteries

Hard carbons have small graphitic grains with disordered orientation, and are much less relevant to exfoliation. These grains also have nanovoids between

Table 2. Graphene properties compared with other carbonaceous materials.

	Graphene	Carbon nanotube	Fullerene	Graphite
Dimensions	2	1	0	3
Hybridization	<i>sp</i> ²	Mostly <i>sp</i> ²	Mostly <i>sp</i> ²	<i>sp</i> ²
Hardness	Highest (for single layer)	High	High	High
Tenacity	Flexible, elastic	Flexible, elastic	Elastic	Flexible, non-elastic
Experimental				
Specific surface area (m ² ·g ⁻¹)	~1500	~1300	80 - 90	~10 - 20
Electrical conductivity (S·cm ⁻¹)	~2000	Structure-dependent	10 ⁻¹⁰	Anisotropic: 2 - 3 × 10 ⁴ *, 6†
Thermal conductivity (W·m ⁻¹ ·K ⁻¹)	4840 - 5300	3500	0.4	Anisotropic: 1500 - 2000*, 5 - 10†

them, resulting in reduced isotropic volume expansion. Nanovoids and defects in hard carbons result in theoretical capacity greater than 372 mAh·g⁻¹ and excess gravimetric capacity. These properties make hard carbons a high capacity high cycle life material. However, hard carbon has high fraction of exposed edge planes which increases absolute quantity of SEI formed and reducing the coulombic efficiency in the first few cycles. Additionally, the void spaces in the grains of hard carbon significantly reduce the density of the particles, further decreasing volumetric capacity [2].

Hard carbon can form composite with Si to increase the capacity of Li⁺ batteries. Kim *et al.* successfully dispersed nanocrystalline Si (*c*-Si) in amorphous Si (*a*-Si) encapsulating hard carbon (HC) as an anode material for fast chargeable lithium-ion batteries. The HC-(*c*-Si)-(a-Si) anode shows excellent cycle retention 97.8% even after 200 cycles at a 1 °C discharge/charge rate. Furthermore, the Li-CoO₂/HC-(*c*-Si)-(a-Si) full-cell showed excellent rate capability and very stable long-term cycle. Even at a rate of 10 °C discharge/charge, the capacity retention of the full-cell was 50.8% of its capacity and showed superior cycle retention of 80% after 160 cycles at a rate of 1 °C discharge/charge, which indicates the possibility of its practical application [18].

3.2. Silicon Based Anode Nanomaterials for Lithium Ion Batteries

Silicon has attracted attention of many researchers due to its excellent feature such as high theoretical specific capacity, higher safety and stability than graphite (lithiated silicon is more stable in typical electrolyte than lithiated graphite). Si anode materials suffer from some drawbacks such as: drastic volume change while the alloying/de-alloying reactions of Li ion, the intrinsic low electrical conductivity, and the unstable solid electrolyte interphase (SEI) formed in the common electrolyte of LiPF₆ [19].

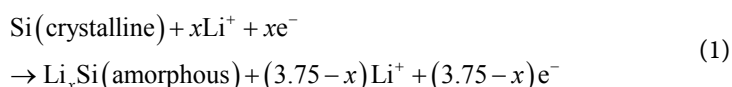
3.2.1. Pure Si Nanostructures

Si-based bulk materials exhibited a marked loss of capacity in a few cycles. Diverse Si nanostructures have been developed to improve the absolute volume change during charging/discharging process. The improvement can be result in shortening of lithium ion diffusion distance and enhancing the electro activity toward Li uptake/release. Controlling the morphology and size of nanowires makes the structure to have good cycling stability. The limited nanowire diameter allows for better accommodation of the large volume change and provides 1D electronic pathways allowing for efficient charge transport. The Si nanowires display high capacities at higher current density. Even at 1 °C rate, the capacities remains 2100 mAh·g⁻¹, and a reversible capacity of over 3000 mAh·g⁻¹ is maintained after 10 cycles [20].

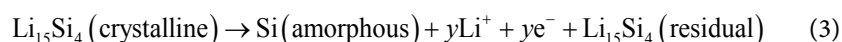
Two-dimensional (2D) Si thin film is another promising nanostructure with improved cycle stability and rate capabilities. Basically, nanosized thin film can minimize the volume variation and retain structural integrity. The cycling stability and the Li accommodation capacity mainly depend on the film thickness as thinner films offer larger accommodation capacity. A 50 nm-thick Si film was found to give a charge capacity over 3500 mA h·g⁻¹ and maintained during 200 cycles at a rate of 2 °C, while a 150 nm-thick film showed around 2200 mAh·g⁻¹ during 200 cycles at 1 °C in the electrolyte of 1 mol/L LiClO₄ in polyethylene carbonate. Although Si thin films offer high specific capacity, good capacity retention and fast charge/discharge rate, the practical application is limited because of their prohibitively high synthesis costs for industry and low active material content [19].

The mechanism of electrochemical lithiation of Si is critical to improve the performance of Si anode. In order to find out the lithiation mechanism, X-ray diffraction (XRD) analysis was performed to investigate the phase transition, and the reaction mechanism is explained as follows [20]:

During discharge:



During charge:



3.2.2. Si/Metal Oxide Composites

McCormac *et al.* encapsulated Si nanoparticles within a highly porous TiO₂ nanofiber matrix using a unique sulphur-templating method combined with electrospinning. After electrochemical characterization, it was determined that the Si/TiO₂ composite nanofibers have specific surface area as large as 387 m²·g⁻¹ and the outside porous TiO₂ nanofiber matrix is able to compensate for 300% volume expansion during the Si lithiation/delithiation process. Therefore,

Si/TiO₂ porous nanofibers have high electrochemical performance, which gives a stable specific capacity of above 1586 mA h·g⁻¹ even after 180 cycles at 0.135 A·g⁻¹ [21].

Molybdenum oxide (MoO₃) is also a potential durable material which forms composite with Si because of little chemical and mechanical degradation during repeated lithium ion insertion and de-insertion. Martinez-Garcia *et al.* designed a silicon decorated MoO₃ nanoplatelet composite material using a hot wire chemical vapor deposition and ultrasonic spray method, which is desirable to realize a high rate and durable, binder free anode in lithium-ion batteries. The specific capacity of the synthesized silicon decorated MoO₃ started at 1475 mA h·g⁻¹ and dropped to about 1000 mA h·g⁻¹ at a cycling rate of 100 mA·g⁻¹ in the second cycle, and then it retained this capacity for over 50 cycles. Even at a high current rate of 10 mA·g⁻¹, the charge capacity in the silicon sprayed MoO₃ composite remained above 1037 mA h·g⁻¹ after 50 cycles, which means there is almost no steady state capacity fading during cycling [18].

3.2.3. Si/C Composites

The combination of Si and carbon materials can highly improve the specific capacity, cycle stability and rate capability for LIBs. Kim *et al.* prepared silicon/carbon composite (Si-C) by thermal decomposition and subsequently formed three-dimensional (3D) electrode structures by the laser ablation process. This 3D Si-C electrode with a conformal carbon coating and empty voids is effective in mitigating large volume expansion and achieving a stable cycling performance. The increased performance exhibited a high specific capacity (>1200 mA h·g⁻¹ over 300 cycles) and good rate capability (1170 mA h·g⁻¹ at 8 A·g⁻¹) [22].

The specific capacity and cyclability of nanostructured Si-C composite electrodes are measured by constant discharge/charge testing. The Si-C electrode delivered a discharge capacity of about 2000 mAh·g⁻¹ in the first cycle, but with an irreversible capacity of about 550 mAh·g⁻¹. Part of this irreversible capacity is used to form a SEI layer on the surface of the negative electrode. The reversible capacity was improved from the second cycle [23].

3.2.4. Si/Graphene Composite

Silicon nanoparticles coated with graphene have become a promising candidate as LIB anode, due to the large surface area, mechanical flexibility, chemical stability and excellent conductivity of graphene. The reversible specific capacity of Si composites can reach 1500 mAh·g⁻¹ after 200 cycles. A very stable cycling performance of the composite has been observed. The capacity remains 1205 mAh·g⁻¹ even after 150 cycles [24].

The cycle performances of anode of different composites of Si nanoparticles and graphene ratios are recorded and visibly at a rate of 100 mA·g⁻¹, all composites have better capacity retention than the Si nanoparticles or graphene, because of better dispersion of Si nanoparticles in the graphene sheet. The synthe-

sis process leads the Si nanoparticles dispersing well on the graphenes, which guarantees that there is abundant interspace between the Si nanoparticles. The abundant interspace can accommodate the volume change of Si nanoparticles in the charge/discharge processes effectively, which also keeps the Si-based anodes to maintain stable in cycling [10].

The composite of 65% Si nanoparticles exhibits the highest capacity after 40 cycles. The high reserve rate of sample 65% Si nanoparticles after 40 cycles is a significant improved property compared with other Si and graphene composite materials. Only the composite with weight ratios of 65:35 has the highest capacity after 40 cycles. This means that the cycle performances of the Si nanoparticles/graphene composite are visibly influenced by the concentration of the graphenes in the composite, which affects the Si nanoparticles dispersion severely. The materials exhibit a low capacity when there are more graphenes due to the lower content of Si nanoparticles. On the contrary, the materials have a larger initial capacity. But the capacity decreases gradually, because there are not enough graphenes to construct the frame work, resulting in the Si nanoparticles aggregating. Thus, the material of 65% Si nanoparticles/35% graphene composite has the highest initial capacity [24].

This indicates that the 65% Si nanoparticles 35% graphene composite has good cycling performance, and the capacity retention after 20 cycles is 96.72%. The initial capacity of the sample 65% Si nanoparticles is $1354 \text{ mA}\cdot\text{g}^{-1}$, and this value falls to $1271 \text{ mA}\cdot\text{g}^{-1}$ at the second cycle. Then, it keeps above $850 \text{ mA}\cdot\text{g}^{-1}$ at the 100th cycle. This is because parts of the active materials are not completely utilized during the first cycles, and they are activated along with the charge/discharge process, which makes the diffusion path of Li^+ wider and results in the capacity enhancement of the material. The structure of composites results in excellent cycle performances [25].

3.3. Tin Based Anode Nanomaterials for Lithium Ion Batteries

Sn anode research is different from Si and Ge anodes in that much focus has been placed on oxides, which showed significantly improved cycle stability. In the fully lithiated state, Sn forms $\text{Li}_{22}\text{Sn}_5$, which places its theoretical capacity limit at $990 \text{ mAh}\cdot\text{g}^{-1}$. While Sn specific capacity is significantly less than that of Si, its volumetric capacity is comparable. However, the theoretical capacity of pure Sn has not been achieved with stable cycling, possibly due to the brittleness of the fully lithiated phase [26]. Many tin-based intermetallics and their composites have been examined as lithium storage materials and have shown increased long-term cycling stability compared to metallic Sn. These intermetallics include Cu_6Sn_5 , SnSb , CoSn_3 , CoSn , Co_3Sn_2 , CoSn_2 , Ni_3Sn_4 , Sn_2Mn , LaSn_3 , Ag_3Sn , SnAg_4 , Mo_3Sn , Ti_xSn_y , Mg_2Sn , SnMn_3C , Sn_2Fe , FeSn , Fe_2Sn_3 , Fe_3Sn_5 and V_2Sn_3 . Even though the electrochemical performance of many of these materials is no better than that of graphite, some of them or their composites have exhibited interesting properties. Cu_6Sn_5 , as an inactive/active intermetallic has been widely used as

an alternative anode material for rechargeable lithium ion batteries [27].

The specific capacities of the as-deposited and post heat-treated composite samples were 534 and 737 mAh·g⁻¹, respectively at the 70th cycle and the corresponding energy densities of the as-deposited and heat-treated composites were 1240 and 1760 Wh/kg, respectively. This enhancement in electrochemical behavior of tin oxide and graphene composites relative to pure tin oxide films is attributed from the addition of graphene [28].

3.3.1. Pure Tin Anode

The theoretical capacity of pure Tin is three times that of the graphite anode (372 mAh/g), based on the end lithiated phase Li₄Sn. Later, crystallographic studies suggested that the realistic form of this end phase could be Li₁₇Sn₄ (thus, 4.25 Li per Sn). Therefore, its maximum gravimetric capacity could be 959.5 mAh·g⁻¹, which is still much higher than most common graphite anodes. Also, the potential of the tin-based anodes is slightly higher than that of graphite, which reduces the potential safety problems with dendrite formation on the host anode, during rapid charging and discharging. Unfortunately, they are affected by the large volume change of these metals during lithium insertion/extraction [1].

Whittingham group demonstrate, pure tin foil (bulk) can be cycled as 600 mAh·g⁻¹ for 10 to 15 deep cycles. However, the expansion and contraction of the electrode crystalline lattice cause some breaking-up of the material. Consequently, the loss of electronic contact between active materials and the current collector dramatically decreases the reversible capacity after 15 cycles. In order to overcome these effects, nanostructures or nanocomposite have been extensively applied [3].

3.3.2. Tin/Carbon Composite

Kim *et al.* reported Sn/C composite by infiltrating tetraethyltin into mechanically milled polystyrene resin powder. The obtained composite has a capacity of 480 mAh·g⁻¹ with good capacity retention over 30 cycles. Recently, Hassoun *et al.* were able to synthesize carbon-tin composites by infiltration of a tin precursor into an organic gel, followed by calcination under argon. Uniform dispersed tin particles were found in the carbon matrix. The particle size of tin was around 50 nm at the surface and less than 10 nm in the bulk. Also, a small amount of residual SnO₂ (8.8%) are found in the composite. properly designed nano-composites show excellent cycling performance. At a 0.8°C rate, the electrode delivers a specific capacity on the order of 500 mAh·g⁻¹ and remains stable over more than 200 cycles. At 5°C rate, the composite recovered 200 mAh·g⁻¹, which is about 40% of its total capacity. Later, Scrosati *et al.* further improved the synthesis procedures and obtained a pure tin compound without a trace of tin oxide. The tin component in the composite is highly stable stored in open air without undergoing any decomposition, because of the protective carbon matrix. The high purity Sn-C composite delivers a reversible and stable capacity on the order of 450 mAh·g⁻¹ [10].

3.3.3. Tin-(M)-Carbon (M = Co, Fe, Ti)

Sn-Co exists as 5-nm particles encapsulated in carbon, which most likely used to prevent much contact between the electrolyte and the metal. Thus, few side reactions happened during electrochemical cycling. The electrochemical behavior of the crystalline tin anode was found to be inferior to that of amorphous tin-based materials. Heating the sample in H₂/He atmosphere can crystallize the Sn-Co amorphous material and also maintain carbon content. The crystallization primarily happened at 300°C. When the amorphous Sn-Co carbon composite were heated to 250°C, the capacity of the material was about 300 mAh·g⁻¹ for the initial cycle and rapidly dropped to about 200 mAh·g⁻¹ after 10 cycles. After heating to 450°C, the capacity is only about 50 mAh·g⁻¹. Despite its remarkable performance, cobalt is expensive and toxic [1].

Recently, the Whittingham group reported Sn/Fe/C composite prepared by mechanical milling using Ti, Al and Mg as the reducing agent and different grinding media. The specific capacity of 600 mAh·g⁻¹, close to the theoretical capacity, was obtained on titanium reduced Sn-Fe carbon composite with good capacity retention on cycling 200 cycles. Also, Sn-Fe-carbon composite has a comparable rate capability with Sn-Co-C materials at a current density of 5 mA/cm². It still can achieve a specific capacity of 250 mAh·g⁻¹ when charged and discharged between the 0.01 - 1.5 V voltage [10].

3.4. Metal Oxide Based Anode Nanomaterials for Lithium Ion Batteries

Transition metal oxides are found to be potential substitutes for graphite as anode materials in LIBs due to their wide ranging electronic, chemical and mechanical properties. Nowadays much interest has been aroused in nanostructured TiO₂ for obtaining fast lithium insertion/removal due to its excellent safety, stability and cost effectiveness [21].

There are two types of reaction mechanisms between transition metal oxides and Li ions:

- ✓ Insertion reaction mechanism: $MO_x + yLi^+ + ye^- \leftrightarrow Li_yMO_x$;
- ✓ Conversion reaction mechanism: $M_xO_y + 2yLi^+ + 2ye^- \leftrightarrow xM + 2yLi_2O$.

Although these transition oxides are cheap and non-toxic, the amount of Li ions inserting themselves into the vacancies of their structures is less than that of the transition metal oxide molecular, which means the insertion reaction-based transition metal oxide can only provide limited specific capacity. For instance, the theoretical specific capacity of TiO₂ is 335 mAh·g⁻¹ (lower than that of graphite), even though it can offer excellent rate capability [7].

Other transition metal oxides that could react with Li⁺ are Fe, Co, Ni, Mn, Cu, Ru, Mo *etc.* Li₂O component will be generated after the conversion reactions between transition metal oxides and Li⁺ ions, and then reversibly recovered to its initial state. With the high oxide state, transition metal oxides can deliver high specific capacities (more than 800 mAh/g) because of multiple electrons involved in the conversion reactions. There is one disadvantage for transition met-

al oxides performing as anodes. Low Coulombic efficiency has always plagued transition metal oxides because of the unstable solid electrolyte interface (SEI). Unlike the uniform SEM layer of carbon based materials, the SEI layer on transition metal oxides is easily destroyed by the large volume changes during cycling. Therefore, to achieve reliable cycling performance and high Coulombic efficiency, there are several approaches, such as decreasing the particle size, forming the deliberated designed porous structure, loading on conductive and flexible host (graphene, CNT or porous carbon based materials) [3].

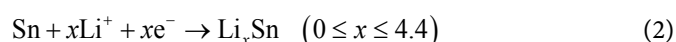
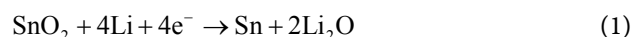
Nanostructured metal oxides exhibit good electrochemical properties, and they are regarded as promising anode materials for high-performance LIBs. Three different categories of metal oxides nanomaterials with distinct lithium storage mechanisms classified as follows:

- Tin dioxide (SnO_2), which utilizes alloying/dealloying processes to reversibly store/release lithium ions during charge/discharge.
- Titanium dioxide (TiO_2), where lithium ions are inserted/deinserted into/out of the TiO_2 crystal framework.

Transition metal oxides including iron oxide and cobalt oxide, which react with lithium ions via an unusual conversion reaction.

3.4.1. SnO_2 Nanomaterials for High-Capacity LIBs

Sn-based materials have drawn much attention as alternative LIB anodes in both the scientific community and industry. SnO_2 has been demonstrated to be one of the most promising anode materials for high performance LIB due to its high theoretical specific storage capacity ($782 \text{ mAh}\cdot\text{g}^{-1}$), compared with the commercially used graphite ($372 \text{ mAh}\cdot\text{g}^{-1}$) [29]. As a representative material for this category, SnO_2 shows attractive lithium storage properties based on the following two reactions:



Reaction (1) is generally considered as irreversible, although it has been suggested to be partially reversible in some studies. The alloying/dealloying reaction described by reaction (2) endows SnO_2 with the capability to accommodate maximally 4.4 Li per Sn, corresponding to a theoretical specific capacity of $790 \text{ mA h}\cdot\text{g}^{-1}$ [30].

3.4.2. TiO_2 Nanomaterials for High-Power LIBs

Titanium dioxide (titania) anode is a very promising material for applications in the LIBs field, and suitable for mass production, cost effective, and TiO_2 has admirable advantages such as high electro-activity, strong oxidation capability, good chemical stability, high abundance and structural diversity. Also, TiO_2 shows excellent safety and stability characteristics at the working potential of 1.5 V vs. Li/Li^+ . These characteristics make TiO_2 a good anode material in LIBs, especially for HEV applications. Titania can host 1 mol of lithium per 1 mol of

TiO₂ with a theoretical maximum capacity of 330 mAh·g⁻¹. The lithium intercalation/de-intercalation process depends on its crystallinity, particle size, structure and surface area. Titania has many allotropic forms; the most well-known are rutile and brookite. Even though anatase titania has been considered the most electroactive form, other allotropes are also widely studied for anode purposes [31].

Decreasing the particle size of rutile form of TiO₂ to 15 nm allows a larger capacity of 378 mAh·g⁻¹ at first discharge and subsequent stable capacity of 200 mAh·g⁻¹ (0.6 Li per one molecule of rutile TiO₂) over 20 cycles, at the current density of 0.05 A·g⁻¹. With particle size of 300 nm, the initial and the 20th cycle capacities of 110 and 50 mAh·g⁻¹ were observed, respectively. The improvement of the capacity and the Li-ion uptake are related to the nanosize characteristic and to the high surface area. Similarly, it was reported that 6 nm particle size of TiO₂ anatase maintains high capacity at more than 200 mAh·g⁻¹ over 20 cycles at the current density of 0.1 A·g⁻¹. Furthermore, at the current rate of 10 A·g⁻¹, the capacity of 125 mAh·g⁻¹ was attained. Moving to higher particle sizes of TiO₂, such as 15 nm and 30 nm, make the lithium ion battery to have lower capacities of 80 and 71 mAh·g⁻¹, respectively [32].

Lee's research group synthesized anatase TiO₂ microspheres by solvothermal process. These TiO₂ microspheres are formed by the combination of ultra-fine 6 - 8 nmTiO₂ nanocrystals with 4 - 6 nm pore size microstructures. The performances of TiO₂ microspheres are increased and it has high lithium storage capability, high number of charging discharging cycles and high tap density. This characteristic improve the capacity, the rate capability as well as the cycling life of titania based anodes. For instance, *Gentili et al.* synthesized nanotube of anatase TiO₂ with wall thickness of 2 - 3 nm, an external diameter of 8 - 10 nm and length in the range 100 - 300 nm. The synthesized nanotubes exhibited maximum capacity at around 300 mAh·g⁻¹ with lithium uptake roughly 0.98 Li for unit formula of titania. Along with high capacity, these titania nanotubes showed high rate capability and good cycling life with a capacity around 250 mAh·g⁻¹ over 100 charge-discharge cycles. Similarly, *Brown et al.* have synthesized mesoporous TiO₂-B microspheres, with 12 nm pore size. This porous titania has proved to be a good anode material at different current densities. Interestingly, a lithium storage capacity of 120 mAh·g⁻¹ was attained at the high current rate of 60°C. This improved rate performance was related to the fast kinetics from the pseudo capacitive electrochemical behavior of microspheres of TiO₂-B [31].

Further development of TiO₂ in terms of power density and cycling life can be achieved by combining titania nanostructures with with other nanostructure materials such as carbon, CNTs and graphene. The obtained specific capacity of this composite was more than 300 mAh·g⁻¹ in the potential range from 1.0 to 3.0 V vs. Li/Li⁺, and stability of these composites was proved over few thousands of charge discharge cycles, from low to high currents, namely from 10 mA·g⁻¹ - 8000 mA·g⁻¹, along with very good columbic efficiency. These promising results were possible due to the nanotubes morphology and to the electronic interac-

tions between the hybrid components [33].

4. Conclusion

Li-ion batteries have become a prominent technology in the global battery market and are currently manufactured in large scale production to be used in small electronic devices, such as cellular phones, portable computers and mobile electro-optic equipment. Due to their high power and energy density they are also good candidates for automotive applications. There are different types of Li-ion batteries based on different anode materials, cathode materials, electrolytes and separators. Graphite and LiCoO_2 are the well known anode and cathode materials respectively, which used lithium ion batteries. In order to improve the capacity of batteries different researchers can synthesize many materials which used as electrodes. Recently, in addition to graphite, there are many alternative materials used as anodes, such as CNT, graphene, porous carbon, metal (Sn, In, etc.), metalloids (Si, Sb and Ge, etc.) and transition metal oxides (Fe, Mn, Ni, Cu and Co, etc.). In order to further improve the theoretical capacity of anodes in lithium ion batteries, different nanomaterials and their composite can be used. Nanomaterials can improve the capacity of lithium ion batteries because it decreases the diffusion distance of electrodes, and increase surface volume ratio of electrodes. The most commonly used anode materials in lithium ion batteries are: carbon silicon, tin, and metal oxide based nanomaterials. Composite of these nanomaterials can further improve the capacity of lithium ion batteries than single nanomaterial. Lithium ion batteries still now have limitation applying to large electric vehicles, in order to improve these problems or to increase the capacity of anode materials much research is going on.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Funding Statement

There is no funding contribution from the agency. The authors are grateful to Department of Chemistry, Mizan tepi University for doing this review work.

Authors' Contributions

Arul Jeevan and Gashaw Tadele, contributed equally to this work.

Acknowledgements

We would like to acknowledge Mizan Tepi University for its financial support.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Chen, J. (2013) Recent Progress in Advanced Materials for Lithium Ion Batteries. *Materials*, **6**, 156-183. <https://doi.org/10.3390/ma6010156>
- [2] Nitta, N., Wu, F., Lee, J.T. and Yushin, G. (2015) Li-Ion Battery Materials: Present and Future. *Materials Today*, **18**, 252-264. <https://doi.org/10.1016/j.mattod.2014.10.040>
- [3] Lahiri, I. and Choi, W. (2013) Carbon Nanostructures in Lithium Ion Batteries: Past, Present, and Future. *Critical Reviews in Solid State and Materials Sciences*, **38**, 128-166. <https://doi.org/10.1080/10408436.2012.729765>
- [4] Wang, G.P., *et al.* (2008) The Effect of Different Kinds of Nano-Carbon Conductive Additives in Lithium Ion Batteries on the Resistance and Electrochemical Behavior of the LiCoO₂ Composite Cathodes. *Solid State Ionics*, **179**, 263-268. <https://doi.org/10.1016/j.ssi.2008.01.015>
- [5] Groot, J. (2012) State-of-Health Estimation of Li-Ion Batteries: Cycle Life Test Methods. Thesis, Chalmers University of Technology, Göteborg, 5.
- [6] Pan, X. (2015) Tin Nanoparticles Encapsulated in Hollow TiO₂ Spheres as High Performance Anode Materials for Li-Ion Batteries. Thesis, University of Wisconsin-Milwaukee, Milwaukee, 3.
- [7] Chen, S. (2014) Novel Nanomaterials for Lithium Ion Batteries and Lithium Sulfur Batteries. Doctoral Dissertation, University of Technology Sydney, Sydney, 10-11.
- [8] Zhao, N., Fu, L., Yang, L., Zhang, T., Wang, G., Wu, Y. and van Ree, T. (2008) Nanostructured Anode Materials for Li-Ion Batteries. *Pure and Applied Chemistry*, **80**, 2283-2295. <https://doi.org/10.1351/pac200880112283>
- [9] Pomerantseva, E., Gerasopoulos, K., Chen, X., Rubloff, G. and Ghodssi, R. (2012) Electrochemical Performance of the Nanostructured Biotemplated V₂O₅ Cathode for Lithium-Ion Batteries. *Journal of Power Sources*, **206**, 282-287. <https://doi.org/10.1016/j.jpowsour.2012.01.127>
- [10] Mauger, A. and Julien, C.M. (2015) Nanoscience Supporting the Research on the Negative Electrodes of Li-Ion Batteries. *Nanomaterials*, **5**, 2279-2301. <https://doi.org/10.3390/nano5042279>
- [11] Lahiri, I. and Wonbong Ch. (2013) Carbon Nanostructures in Lithium Ion Batteries: Past, Present, and Future. *Critical Reviews in Solid State and Materials Sciences*, **38**, 128-166. <https://doi.org/10.1080/10408436.2012.729765>
- [12] Sneha, T., *et al.* (2015) Carbon Nanotube Based Paper Battery and Lithium Ion Battery. *International Journal of Application or Innovation in Engineering & Management (IJAIEEM)*, **4**, 179-181.
- [13] Li, L., Yang, H., Zhou, D. and Zhou, Y. (2014) Progress in Application of CNTs in Lithium-Ion Batteries. *Journal of Nanomaterials*, **2014**, Article ID: 187891. <https://doi.org/10.1155/2014/187891>
- [14] Xiong, Z., Yun, Y.S. and Jin, H.J. (2013) Applications of Carbon Nanotubes for Lithium Ion Battery Anodes. *Materials*, **6**, 1138-1158. <https://doi.org/10.3390/ma6031138>
- [15] Zhu, J., Duan, R., Zhang, S., Jiang, N., Zhang, Y. and Zhu, J. (2014) The Application of Graphene in Lithium Ion Battery Electrode Materials. *SpringerPlus*, **3**, Article No. 585. <https://doi.org/10.1186/2193-1801-3-585>
- [16] Sui, Z., Wang, C., Yang, Q., Shu, K., Liu, Y., Han, B. and Wallace, G.G. (2015) A Highly Nitrogen-Doped Porous Graphene—An Anode Material for Lithium Ion Batteries. *Journal of Materials Chemistry A*, **3**, 18229-18237. <https://doi.org/10.1039/C5TA05759K>

- [17] Raccichini, R., Varzi, A., Passerini, S. and Scrosati, B. (2015) The Role of Graphene for Electrochemical Energy Storage. *Nature Materials*, **14**, 271-279. <https://doi.org/10.1038/nmat4170>
- [18] Wang, J., Xu, T., Huang, X., Li, H. and Ma, T. (2016) Recent Progress of Silicon Composites as Anode Materials for Secondary Batteries. *RSC Advances*, **6**, 87778-87790. <https://doi.org/10.1039/C6RA08971B>
- [19] Yin, Y., Wan, L. and Guo, Y. (2012) Silicon-Based Nanomaterials for Lithium-Ion Batteries. *Chinese Science Bulletin*, **57**, 4104-4110. <https://doi.org/10.1007/s11434-012-5017-2>
- [20] Ma, D., Cao, Z. and Hu, A. (2014) Si-Based Anode Materials for Li-Ion Batteries: A Mini Review. *Nano-Micro Letters*, **6**, 347-358. <https://doi.org/10.1007/s40820-014-0008-2>
- [21] Chen, C., Agrawal, R. and Wang, C. (2015) High Performance Li₄Ti₅O₁₂/Si Composite Anodes for Li-Ion Batteries. *Nanomaterials*, **5**, 1469-1480. <https://doi.org/10.3390/nano5031469>
- [22] Li, X.Z., Wang, X.H., Li, S.W. and Qiu, X.P. (2014) A Novel Silicon/Carbon Nanocomposite Anode for High Performance Lithium-Ion Micro-Battery. *Journal of Physics: Conference Series*, **557**, Article ID: 012059. <https://doi.org/10.1088/1742-6596/557/1/012059>
- [23] Wang, G. X., *et al.* (2004) Nanostructured Si-C Composite Anodes for Lithium-Ion Batteries. *Electrochemistry Communications*, **6**, 689-692. <https://doi.org/10.1016/j.elecom.2004.05.010>
- [24] Su, X., Wu, Q., Li, J., Xiao, X., Lott, A., Lu, W., Sheldon, B.W. and Wu, J. (2014) Silicon-Based Nanomaterials for Lithium-Ion Batteries: A Review. *Advanced Energy Materials*, **4**, Article ID: 1300882. <https://doi.org/10.1002/aenm.201300882>
- [25] Chen, Y., Zhang, X., Tian, Y. and Zhao, X. (2014) Synthesis and Characterization of Silicon Nanoparticles Inserted into Graphene Sheets as High Performance Anode Material for Lithium Ion Batteries. *Journal of Nanomaterials*, **2014**, Article ID: 734751. <https://doi.org/10.1155/2014/734751>
- [26] Nitta, N. and Yushin, G. (2014) High-Capacity Anode Materials for Lithium-Ion Batteries: Choice of Elements and Structures for Active Particles. *Particle & Particle Systems Characterization*, **31**, 317-336. <https://doi.org/10.1002/ppsc.201300231>
- [27] Kamali, A.R. and Fray, D.J. (2011) Tin-Based Materials as Advanced Anode Materials for Lithium Ion Batteries: A Review. *Reviews on Advanced Materials Science*, **27**, 14-24.
- [28] Dhanabalan, A., Li, X., Agrawal, R., Chen, C. and Wang, C. (2013) Fabrication and Characterization of SnO₂/Graphene Composites as High Capacity Anodes for Li-Ion Batteries. *Nanomaterials*, **3**, 606-614. <https://doi.org/10.3390/nano3040606>
- [29] Zhao, Q., Ma, L., Zhang, Q., Wang, C. and Xu, X. (2015) SnO₂-Based Nanomaterials: Synthesis and Application in Lithium-Ion Batteries and Supercapacitors. *Journal of Nanomaterials*, **2015**, Article ID: 850147. <https://doi.org/10.1155/2015/850147>
- [30] Wu, H.B., Chen, J.S., Hng, H.H. and Lou, X.W. (2012) Nanostructured Metal Oxide-Based Materials as Advanced Anodes for Lithium-Ion Batteries. *Nanoscale*, **4**, 2526-2542. <https://doi.org/10.1039/c2nr11966h>
- [31] Goriparti, S., Miele, E., Angelis, D.F., Fabrizio, D.E., Zaccaria, P.R. and Capliga, C. (2014) Review on Recent Progress of Nanostructured Anode Materials for Li-Ion Batteries. *Journal of Power Sources*, **257**, 421-443. <https://doi.org/10.1016/j.jpowsour.2013.11.103>

- [32] Han, X., Ouyang, M., Lu, L. and Li, J. (2014) Cycle Life of Commercial Lithium-Ion Batteries with Lithium Titanium Oxide Anodes in Electric Vehicles. *Energies*, **7**, 4895-4909. <https://doi.org/10.3390/en7084895>
- [33] Han, C., Yang, D., Yang, Y., Jiang, B., He, Y., Wang, M., Song, A., He, Y, Li, B. and Lin, Z. (2015) Hollow Titanium Dioxide Spheres as Anode Material for Lithium Ion Battery with Largely Improved Rate Stability and Cycle Performance by Suppressing the Formation of Solid Electrolyte Interface Layer. *Journal of Material Chemistry*, **3**, 13340-13349. <https://doi.org/10.1039/C5TA02070K>