Bismuth Chalcogenide Compounds Bi_2X_3 ($\text{X} = \text{O}, \text{S}, \text{Se}$): Applications in Electrochemical Energy Storage

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Abstract Bismuth chalcogenides Bi_2X_3 ($\text{X} = \text{O}, \text{S}, \text{Se}$) represent a unique type of materials in diverse polymorphs and configurations. Multiple intrinsic features of Bi_2X_3 such as narrow bandgap, ion conductivity, and environmental friendliness, have render them attractive materials for a wide array of energy applications. In particular, their rich structural voids and the alloying capability of Bi enable the chalcogenides to be alternative electrodes for energy storage such as hydrogen (H), lithium (Li), sodium (Na) storage and supercapacitors. However, the low conductivity and poor electrochemical cycling are two key challenges for the practical utilization of Bi_2X_3 electrodes. Great efforts have been devoted to mitigate these challenges and remarkable progresses have been achieved, mainly taking profit of nanotechnology and material compositing engineering. In this short review, we summarize state-of-the-art research advances in the rational design of diverse Bi_2X_3 electrodes and their electrochemical energy storage performance for H, Li, and Na and supercapacitors. We also highlight the key technical issues at present and provide insights for the future development of bismuth based materials in electrochemical energy storage devices.

1. INTRODUCTION

Bismuth (Bi) is a post-transition metal element, chemically resembling its lighter homologs arsenic and antimony (Figure 1). Although elemental bismuth is sparsely found in nature, its chalcogenides such as oxide and sulfide are important ores for commercial use. The elemental Bi is a brittle metal with a silvery white color when freshly produced. It is usually seen as a pink tinge because of surface oxidation in air. Bi has many unusual properties such as the low melting point, the lowest thermal conductivity among metals, and volume expansion upon freezing, which endow Bi with unique applications in electronics and printing. More significantly, Bi has a much lower toxicity in comparison to lead, and thus there is an increasing use of bismuth alloys as a replacement for lead.

Bismuth chalcogenides Bi_2X_3 ($\text{X} = \text{O}, \text{S}, \text{Se}$) are important n-type semiconductors for sensors and photocatalysts, owing to their response to light in the visible-light region [1]. Their peculiar characteristics including narrow bandgap, high refractive index, dielectric permittivity, ion conductivity and remarkable photoconductivity have endowed Bi_2X_3 as versatile photocatalyst candidates for water splitting, NO oxidation and particularly, organic pollutant decomposition under visible light irradiation [2]. They also have a huge potential application in photodiode arrays, photovoltaic converters and thermoelectric technology.

1.1. STRUCTURE AND SYNTHESIS OF BISMUTH CHALCOGENIDES

The most common polymorph of bismuth oxide (Bi_2O_3) is the mineral bismite ($\alpha\text{-Bi}_2\text{O}_3$), which crystallizes in the monoclinic P21/c. In this structure, the unit cell contains two Bi (Bi-I and Bi-II) atoms located at 4e sites and three O atoms located at 4e sites. The two Bi atoms have different coordination to O atoms: Bi-I has five-fold coordination while Bi-II has six-fold coordination (Figure 2a) [3]. The structure of Bi_2O_3 depends on the thermal history. Heating $\alpha\text{-Bi}_2\text{O}_3$ above 730 °C results in the formation of $\delta\text{-Bi}_2\text{O}_3$ with the cubic fluorite-type crystal structure, while on cooling, $\delta\text{-Bi}_2\text{O}_3$ is possible to form two intermediate metastable phases: the tetragonal β phase and the body-centered cubic γ phase [4]. Bismuth sulfide (Bi_2S_3) has an orthorhombic structure with the direct band gap ($E_g = 1.3 \text{ eV}$). The crystal structure of Bi_2S_3 consists of a highly anisotropic layer structure with linked infinite ribbon-like Bi_4S_6 unit and each layer, which in turn are connected via weaker van der Waals interactions (Figure 2b). The Bi and S atoms are linked by intermolecular attraction and thus construction of a chain-like building block which is parallel to the c-axis [5]. In the same way, two independent Bi positions can be identified, in which Bi1 is located at the margin of the Bi_4S_6 ribbon and Bi2 around the center of the ribbon [6]. As for the bismuth selenide (Bi_2Se_3), its structure is formed by a periodic arrangement of layers aligned perpendicular to the trigonal c-axis (Figure 2c). Each layer is composed of five atomic planes arranged according to the following

pattern... $\text{Se}^1\text{--Bi--Se}^2\text{--Bi--Se}^1\cdots\text{Se}^1\text{--Bi--Se}^2\text{--Bi--Se}^1\cdots$. Between Se^1 atomic planes of neighboring atoms there is a van der Waals gap. As there are many unoccupied octahedral and tetrahedral in the gap, incorporation of guest species into the Bi_2Se_3 crystal is possible.

The critical electronic and electric properties of Bi_2X_3 are strongly affected by its morphology and depend on the crystal structure. To fulfill the requirements for specific energy application, Bi_2X_3 compounds have been fabricated in versatile structures, shapes, morphologies, dimensions, and sizes via various routes. Bi_2O_3 can be directly prepared by chemical precipitation using solution Bi salt as precursor, but usually suffer from poor crystallinity due to low temperature. To obtain high quality crystals, hydrothermal or solvothermal reactions are frequently adopted [7, 8]. Bismuth oxides can be converted to sulfides and selenides via a facile anion ion exchange process [9, 10]. Due to a layered structure, various Bi_2S_3 and Bi_2Se_3 nanostructures can be easily realized through the crystal splitting [11] or by a chemical vapor transport [12]. Recently, ultrafine colloidal Bi_2S_3 quantum dots [13] and ultrathin Bi_2S_3 nanowires [14] have been prepared through a colloidal solution process. These colloidal nanocrystals provide a unique platform for understanding the growth kinetics of Bi_2X_3 and the bandgap modulation via the quantum size effect.

1.2. INTRINSIC FEATURE OF BISMUTH CHALCOGENIDES FOR ENERGY STORAGE

Electricity is considered the most convenient form of energy source, due to the ease of transport and conversion to other types of energy. However, electricity must be used as it is generated or converted immediately into storable forms, since it cannot be stored. Available energy storage technology that can meet demands whenever needed would represent a major breakthrough in electricity distribution. Many renewable energy sources (notably solar and wind) produce variable power, which requires energy storage devices to make it smooth and distributable [15]. Over the last decade, the energy storage industry has continued to evolve and adapt to change energy requirements and advances in technology [16, 17]. The most frequently used electrochemical systems include hydrogen based fuel cells, rechargeable batteries, and supercapacitors [18, 19]. This is because these solutions manifest a high energy efficiency, low discharge, long lifetime, wide operating temperature range, and low maintenance. One of the biggest challenges facing these ubiquitous solutions is to find efficient electrodes that can store a large amount of hydrogen (H), lithium (Li), and sodium (Na) in a rapid and robust manner.

Two key features can be recognized as bismuth chalcogenides are utilized in electrochemical energy storage. One is that there is sufficient space for intercalant accommodation in their crystalline lattice. In $\alpha\text{-Bi}_2\text{O}_3$, the possible sites for guest ions lie between two successive cationic or anionic layers parallel to the (100) monoclinic planes [4]. As for Bi_2S_3 and Bi_2Se_3 , the interlayer in lattice provides channels for transport and occupation of guest ions. The other feature is that Bi_2X_3 can be

conveniently reduced to metallic Bi, which further alloys with Li and Na ions, generating Li_3Bi and Na_3Bi , respectively [20]. This alloying process is highly reversible and enables a gravimetric capacity of 385 mAh g^{-1} and extremely high volumetric capacity of $\sim 3800 \text{ mAh cm}^{-3}$, due to a large pack density of 9.78 g cm^{-3} [21]. The high volumetric capacity of Bi is essential for rechargeable batteries, because limited space is usually available for the power systems in compact electronic devices. This offers a reliable and multifunctional platform to design energy devices that can meet our growing energy and power demands in the future.

Bi_2X_3 compounds are essential electrode materials for electrochemical energy storage and have been intensively explored over the last decade. Thus, it is useful to summarize the recent advancement on the application of the Bi_2X_3 compounds in energy storage. In this review, we will summarize the state-of-the-art material design and applications of Bi_2X_3 compounds in H, Li, Na storage and supercapacitor, and some newly emerging systems. In view of the fact that metallic Bi is the key intermediate and also the source of high activity and reversibility for energy storage, progress in Li and Na storage in Bi is enclosed. **Bi_2Te_3 is not enclosed in this review because it is structurally instable upon ion accommodation.**

2. APPLICATIONS IN HYDROGEN STORAGE

Hydrogen is one of the key alternatives to replace fossils as a clean energy carrier for stationary and automobile applications [22]. Hydrogen has the highest gravimetric energy, however, its low density results in a low volumetric energy. Therefore, the development of advanced storage technology that have potential for higher energy density is desired, but remains a significant challenge, due to lack of efficient storage materials. Generally, an ideal storage material can store large quantities of hydrogen reversibly and rapidly in the suitable temperature range (room temperature to 120°C). Many storage materials have been exploited for hydrogen, but no single material can fulfill these requirements simultaneously [22, 23].

Bismuth can form bismuth hydride (BiH_3), also known as bismuthine, to store hydrogen, but it is extremely unstable and immediately decomposes to bismuth metal well below 0°C . In most cases, Bi metal is adopted for H production rather than storage because it improves the adsorption of hydrogen on photocatalyst such as Pt [24]. Likewise, Bi_2O_3 serves as photocatalyst for hydrogen production from water splitting under visible light [25]. Naturally, Bi_2S_3 is expected to show outstanding hydrogen storage properties because its inherent lamellar structure. Hydrogen storage in Bi_2S_3 is a step-wise electrochemical process, manifesting two potential plateaus in the charge and discharge profile. The two steps reflect a possible hydrogen storage in two distinct sites: hydrogen was first adsorbed into the nanopores of bulk and then entered into the interlayers of Bi_2S_3 [26]. Notably, Li *et al.* have prepared disk-like Bi_2S_3 nanofabrics via a topotactic transformation of BiOCl precursor

(Figure 3) [27]. When used as the working electrode, the nanofabrics exhibit a hydrogen storage capacity of 162 mAh g^{-1} . In the CV profile, the prominent cathodic peak at -0.72 V (vs. Hg/HgO) is attributed to hydrogen adsorption/reduction, and the two anodic peaks at -0.54 V and -0.40 V due to hydrogen desorption and oxidation, respectively. The overlap of the two anodic processes is a result of fast redox reaction of hydrogen catalyst by Bi_2S_3 . Hydrogen storage is thermodynamically governed, but largely determined by kinetics. Thus, Bi_2S_3 materials with small size, large surface area, and rich mesopores would help to facilitate the storage reaction. Several works have confirmed this point. For instance, well-aligned Bi_2S_3 nanorods exhibit a higher capacity than network-like nanoflakes [26]; Bi_2S_3 nanorod networks have a higher capacity than nanorod bundles [27]. A similar trend has been reported by Wang *et al.* [28] and Hu *et al.* [29], who both observe a significant enhancement in the capacity when Bi_2S_3 nanorods are assembled into nanoflowers, because the latter have many porous sites for hydrogen adsorption. In this regard, Jin *et al.* further explore some Bi_2S_3 hierarchitectures [30, 31], which show a high hydrogen storage capacity due to more interstitial pores that are accessible to hydrogen and integrated structure networks that facilitate electron transport.

Equally, laminar Bi_2Se_3 is a potential H-storage material and may exhibit a capacity greater than Bi_2S_3 . Sun *et al.* have fabricated two kinds of Bi_2Se_3 nanostructures, 3D rose-like hierarchical and monodisperse nanospheres through a thermostatic bath [32]. The 3D rose-like Bi_2Se_3 exhibits a hydrogen storage capacity up to 185 mAh g^{-1} , which is related to the special hierarchitectures with highly crystallized flake-substructures. By analogue, Jin *et al.* could obtain hierarchical $\text{Bi}_2\text{Se}_{3-x}\text{S}_x$ microflowers assembled from ultrathin polycrystalline nanosheets via a solvothermal route [33]. The flower-like $\text{Bi}_2\text{Se}_{3-x}\text{S}_x$ assembly enables a high reversible capacity of 197 mAh g^{-1} , in contrast to 168 mAh g^{-1} for Bi_2Se_3 nanosheets, due to the larger surface area of $28.6 \text{ m}^2 \text{ g}^{-1}$ relative to $5.7 \text{ m}^2 \text{ g}^{-1}$. Also, sulfur doping results in a second charge plateaus at -0.49 V vs. Hg/HgO , while the pristine Bi_2Se_3 only has one plateau at -0.55 V . The two plateaus indicates the energy at which hydrogen is adsorbed is varied after sulfur substitution.

It is worth noting that H storage in bismuth materials remains at a low concentration, which makes them less competitive than other well-developed storage materials such as LaNi_5 , FeTi alloys, and metal-organic frameworks [34]. Moreover, H-storage stability in either Bi_2S_3 or Bi_2Se_3 is a major challenge. In most cases, it hardly sustain 100 cycles with capacity retention above 60%. Further research may focus on the design of ordered porosity to increase the accessible volume and specific nanostructure to boost H adsorption between chalcogenide interlayers, and to achieve highly reversible and sustainable H retention.

3. APPLICATIONS IN LITHIUM STORAGE

The continuous development of electronics and electric vehicles has set a high demand on electrical energy storage systems such as rechargeable batteries and supercapacitors. Currently, Li-ion batteries are one of the most promising systems because of the high energy density, environmental friendliness, and great flexibility. While myriad electrode materials have been explored to further improve the electrochemical performance, significant challenges in terms of low capacity and efficiency remain, which impose critical limitation for the next-generation Li-ion batteries.

3.1 BISMUTH FOR LITHIUM STORAGE

Bi can alloy with Li to produce Li_3Bi alloy, whose volumetric capacity (3.8 Ah cm^{-3}) is more than four-fold that of commercial graphite anodes. Moreover, Li_3Bi alloy occurs at an equilibrium potential of 0.8 V (vs. Li^+/Li), which makes it intrinsically free from lithium plating. The high capacity is attractive but also brings a substantial volume expansion during Li uptake. Formation of Li_3Bi alloy leads to a volume expansion of 110% versus Bi. Naturally, this expansion cannot be mitigated by micron or submicron Bi particles, and substantial pulverization and crack will occur. As pulverized Bi particles cannot be electronically wired by the conducting network, they lose their access to Li, resulting in a drastic capacity fading. To realize a better cycling, Park *et al.* designed Bi/C and Bi/ Al_2O_3 /C nanocomposites, in which Bi nanocrystals were uniformly distributed in amorphous C (or admixture of amorphous Al_2O_3 and C) [21]. As amorphous Al_2O_3 and C might efficiently buffer the stress and strain upon Li uptake in Bi particles, a high capacity of 310 mAh g^{-1} and a remarkable retention of 74% were retained over 100 cycles.

As an alternative strategy, dispersion of Bi particles in an “ion conductive solid-state matrix” can address this cycling limitation issue. Figure 4 illustrates how an ion conductive matrix can minimize particle pulverization and thus achieve a better capacity retention. Sun *et al.* firstly grew graphene wrapped BiPO_4 nanocrystals ($\text{BiPO}_4@\text{G}$), which were then transformed to Bi nanoparticles in a solid-state- Li_3PO_4 matrix via an in situ electrochemical process [35]. The resulting $(\text{Bi}+\text{Li}_3\text{PO}_4)@\text{G}$ composite anode exhibits a reversible capacity of 280 mAh g^{-1} at a rate of 100 mA g^{-1} and a record cyclability among bismuth-based anodes up to 500 cycles (64.5%). Merits using Li_3PO_4 matrix can be considered as follows [35]. First, it functions as a solid binder to keep the Bi grains to be physically interconnected and the structural integrity well-maintained. Second, it is electrochemically stable within a wide potential window, and buffers the mechanical strain arising from the lithium insertion. Third, Li_3PO_4 is a Li^+ ion conductor ($4.5 \times 10^{-5} \text{ S m}^{-1}$) and can provide ion diffusion channels for active Bi grains. Fourthly, it isolates Bi from liquid electrolyte and thus reduces undesirable side reactions such as the formation of solid electrolyte interphase (SEI). This work provides a special insight to design highly stable Bi or other alloy type anodes.

3.2 BISMUTH CHALCOGENIDES FOR LI STORAGE

About thirty years ago, Julien and coworkers investigated the lithium insertion in Bi_2X_3 using several electrochemical methods such as potentiostatic test and linear sweep voltammetry [36]. They observed that the lattice of chalcogenides allowed a limited amount of Li ions inserting reversibly, upon further lithiation, the electrochemical behavior becomes more complex and the material can be reduced into Li_2X . As shown in Figure 5, it is quite clear now that Bi_2X_3 is firstly reduced Li_2X via the reaction $\text{Bi}_2\text{X}_3 + 6\text{Li} \leftrightarrow 3\text{Li}_2\text{S} + 2\text{Bi}$ (Eq. 1), which is followed by the alloying process $\text{Bi} + 3\text{Li} \leftrightarrow 2\text{Li}_3\text{Bi}$ (Eq. 2). Both conversion and alloying reactions contribute to a substantial volumetric augment (i.e. 230% for Bi_2S_3), which is more severe than Bi. As this expansion causes particle cracks and pulverization, a continuous capacity decay is inevitable. Thus, how to improve cyclability of the chalcogenide materials remains a challenge to be addressed for optimization of their Li-storage performance.

Lithium storage in Bi_2O_3 has been examined by Fiordiponti and coworkers in 1978 [20] and revisited recently by Li group, who directly grew bismuth oxide on nickel foam using a polymer-assisted solution approach [37]. This Ni foam supported $\text{Bi}_2\text{O}_3/\text{C}$ film was used directly as an electrode for Li storage. A high capacity of 1211 mAh g^{-1} was obtained, way above the theoretical value of 690 mAh g^{-1} . The additional capacity might come from the carbon network and formation of SEI on the electrode surface. It delivered the capacity of 668 mAh g^{-1} at a high current of 800 mA g^{-1} , but the cycling needed improvement. To achieve a high capacity and cycling, nanocomposites were generally designed and fabricated. Li *et al.* prepared an ordered macroporous Bi_2O_3 sample using polymethyl methacrylate spheres as colloidal crystal template [38]. This sample exhibited a reversible recharge capacity of 500 mAh g^{-1} at a rate of 0.2 C, because the pores provided sufficient space for volume variation upon Li uptake. Fang *et al.* synthesized $\text{Bi}_2\text{O}_3/\text{graphene}$ composite that also showed enhancement in capacity delivery and retention [39]. In another case, Liu *et al.* designed a heterostructure of $\text{Bi}_2\text{O}_3\text{-Bi}_2\text{S}_3$ composite through a partially sulfurization on Bi_2O_3 nanosheets [40]. This heterostructure showed an initial Coulombic efficiency of 83.7%, which is the highest value reported so far for bismuth based materials, thus paving a way towards their practical application. Such an outstanding Li-storage property might arise from the unique heterogeneous nanosheet architecture, which greatly reduced the electron and ion transport length and charge transfer resistance. In addition, the heterostructure also avoided the aggregation of nanosheets and consequently, retaining highly accessible area for Li uptake upon cycling.

Bi_2S_3 has been intensively examined as anode for Li-ion batteries, but the cycling remains a critical issue [41, 42]. This is because Bi_2S_3 suffers from poor electronic conductivity, grain pulverization, and dissolution loss of sulfur species in organic electrolytes. To improve the cyclability, it is predicted to reduce the grain size and integrate Bi_2S_3 into carbonaceous materials [43, 44]. Zhao *et al.* coated Bi_2S_3 nanomeshes by carbon via a hydrothermal route. This composite

retained a capacity of 472 mAh g⁻¹ in the 50th cycle at 120 mA g⁻¹ [45]. Jung *et al.* dispersed Bi₂S₃ nanocrystals in amorphous carbon via a ballmilling method, and achieved a capacity of ~500 mAh g⁻¹ based on the mass of Bi₂S₃ over 100 cycles [46]. The resultant Bi₂S₃/C could Zhang *et al.* synthesized Bi₂S₃/RGO composite and it could remain at 290 mAh g⁻¹ at current density of 1 A g⁻¹ [47]. Very recently, Mai group encapsulated Bi₂S₃ microwires into amorphous SiO₂ [48], and achieved an excellent electrochemical cycling of 379 mAh g⁻¹ after 4000 cycles at a current density of 1 A g⁻¹. They attributed the robust cycle to the mechanically rigid of surface SiO₂, which can buffer the volume change and stabilize the SEI.

Ni *et al.* have developed the nanocomposite by a concept of “strong coupling”. By coupling Bi₂S₃ nanocrystals onto functional carbon nanotube (CNT), they could design highly efficient Bi₂S₃ hybrid electrodes. Two coupling configurations, i.e. the branch structure [49] and the core-sheath structure [50] of Bi₂S₃-CNT have been engineered using bismuth nitrate, CNT and thioacetamide as raw materials through sonochemical approach at ambient temperature. The branch-structured Bi₂S₃-CNT compose of the numerous uniform Bi₂S₃ nanorods vertically attached on the flexible CNT backbones. In the core-sheath hybrid, worm-like Bi₂S₃ overlayer is deposited on the CNT backbones. Variation in the configuration is intimately related to the reaction parameters of temperature and acidity. As both structures are highly porous and tightly attached on the CNT backbone, a facile Li storage kinetic can be realized. The core-sheath hybrid delivers a stable capacity of 502 mAh g⁻¹ at a current of 200 mA g⁻¹ and 468 mAh g⁻¹ at 1 A g⁻¹ over 100 cycles, demonstrating an unprecedented cycling stability (Figure 6). Moreover, this nanocomposite exhibits one of the best rate capabilities among reported Bi₂S₃ materials, affording a capacity of 376 mAh g⁻¹ at 5 A g⁻¹. The superb property verifies that the strong coupling strategy is extremely efficient for electrode materials engineering [19, 51]. Very recently, this group has designed a bio-inspired Bi₂S₃PPy yolk-shell composite, which exhibits a superior Li storage cyclability (99% for 500 cycles) and a high rate capability (337 mAh g⁻¹ at 10 C), outstripping any previous bismuth based materials [52].

Bi₂Se₃ is a promising host for Li storage owing to its high electrical conductivity (10.6 S cm⁻¹ at 300 K) [53, 54], although its theoretical capacity (491 mAh g⁻¹) is slightly lower than Bi₂S₃, due to the large formula weight. Various Bi₂Se₃ nanomaterials have been prepared and tested as Li anode, but none can sustain substantial capacity (> 200 mAh g⁻¹) over 50 cycles [55-57]. The best cycling stability comes from In-doped Bi₂Se₃, which retained 160 mAh g⁻¹ at the 50th cycle [56]. This is because selenides suffer from dissolution loss of selenium species and the volume expansion, as sulfides do. A potential strategy to mitigate the cycling issue is likely to integrate Bi₂Se₃ into nano-carbons [58-60].

4. APPLICATIONS IN NA STORAGE

Li-ion batteries are currently being considered for electric vehicle and even renewable energy, due to their success in powering electronics. However, the scalable implementation of a lithium technology faces controversial debates on the availability and cost of Li resource. As an alternative, Na-ion batteries represent a low-cost and sustainable battery technology that would be specially suited for large scale applications [61, 62]. The most appealing feature of sodium is its rich intercalation chemistry and its in principle unlimited resources (high concentrations in seawater). Although many potential cathodes are available for Na-ion batteries currently, it remains a major challenge to develop anode materials with long cycle life and good rate capability [63-66].

4.1 BISMUTH FOR NA STORAGE

Analogously, Bi reacts with Na to generate Na_3Bi alloy, with the average potential ~ 0.3 V below that of Li_3Bi alloy, because the large Na^+ ions distort the lattice structure and result in an instability of the framework [67]. In addition, formation of Na_3Bi results in an enormous volume augment of $\sim 250\%$, which is much greater than that for Li_3Bi . As a rough estimation, a spherical Bi grain will increase its diameter by 52% for sodiation compared to 28% for lithiation. Therefore, it is rational to believe that both the kinetics and thermodynamics of sodiation in Bi will vary remarkably depending on the crystallite size. Using in operando synchrotron XRD/XAS, Sottmann and coworkers have confirmed that crystallite size controls the reaction path in sodium bismuth alloying, which makes the structural chemistry deviate from what is predicted by the equilibrium phase diagram [68]. As shown in Figure 7, micro-sized Bi grain alloying with Na generates hexagonal Na_3Bi (h- Na_3Bi), just following the thermodynamic prediction. While nano-sized Bi alloying with Na gives rise to metastable cubic Na_3Bi (c- Na_3Bi). The theoretical voltage for $\text{NaBi} \leftrightarrow \text{c-Na}_3\text{Bi}$ is 0.03 V lower than for $\text{NaBi} \leftrightarrow \text{h-Na}_3\text{Bi}$, due to their structural differences. In h- Na_3Bi (Na_3As -type), Na1 and Bi1 form simple 2D honeycomb layers that are stacked along the c-axis and separated by Na2 which are connected to Bi. The vertical Na2–Bi1 bonds between adjacent layers are 3.209 Å. c- Na_3Bi crystallizes with the Li_3Bi -type structure, in which Na2 and Bi1 form a 3D network with interatomic distances of 3.319 Å. The weaker Na–Bi bonds in c- Na_3Bi indicate that less energy is needed during alloying or dealloying process.

The established alloying mechanism has recently been challenged by Su *et al.* [69]. They examined the electrochemical performance and structure evolution of 3D graphene wrapped Bi nanoparticles. At the assistance of ex situ XRD and HRTEM analysis, they claimed that Na storage in bismuth is an intercalation process rather than alloying, because the large interlayer spacing along the c-axis ($d_{(003)} = 0.395$ nm) is capable of accommodate additional Na ions. This argument might be more convincing if in situ tests could be conducted and the effect of graphene on the Na storage taken into

account. From the viewpoint of material engineering, graphene wrapping provided an appealing solution towards efficient Na storage in Bi [69]. The Bi/graphene hybrid supplied a high reversible capacity of $\sim 490 \text{ mAh g}^{-1}$ and retained a capacity of 250 mAh g^{-1} at a high rate of 1280 mA g^{-1} .

4.2 BISMUTH CHALCOGENIDES FOR NA STORAGE

The rising of Na-ion batteries has spurred great interests in exploring the Na-storage capability of bismuth chalcogenides. Most researches leverage the knowledge recently developed on Li storage and the general strategies include nanosizing, substitution, and nano-carbon coating. Bi_2S_3 nanorods achieved a Na capacity of 658 and 264 mAh g^{-1} at a current density of 100 and 2000 mA g^{-1} , respectively [70]. A full cell with the Bi_2S_3 nanorod anode and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode is capable of affording a capacity of 340 mAh g^{-1} at 100 mA g^{-1} (based on the anode) with average working potential of 2.0 V. Graphite coated Bi_2S_3 composite delivered an initial capacity of 550 mAh g^{-1} , with an enhanced capacity retention of 69% over 100 cycles [71]. Similarly, Bi_2O_3 nanoparticles anchored on rGO sheets were prepared [72]. The resultant $\text{Bi}_2\text{O}_3@\text{rGO}$ delivered a reversible capacity of 669 mAh g^{-1} . More importantly, it exhibited a capacity retention of 70.2% over 200 cycles at a rate of 350 mA g^{-1} , representing one of the best results for bismuth based electrodes. Similar material engineering based on graphene wrapping is also reported for antimony electrodes [73, 74].

Zhao and Manthiram reported a binary solid solution anode of $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ with a nanorod cluster morphology (Figure 8) [75]. When coupled with graphite, the simple composite obtained by a mechanical milling of 80 wt% $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ and 20 wt% graphite exhibits much improved cycling with 79% capacity retention after 200 cycles in the full voltage window of 0.01–2.8 V. Under the identical cycling condition, counterparts Bi_2S_3 –graphite and Sb_2S_3 –graphite only display a retention of 58% and 10%, respectively. At very high current densities of 7 and 10 A g^{-1} , the composite electrode delivers, respectively, remarkable charge capacities of 347 and 256 mAh g^{-1} . The polarization overpotential associated with the conversion reaction in $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ is also much lower than those in Bi_2S_3 and Sb_2S_3 , due to the synergistic effect with binary alloy systems. By limiting the cutoff potentials to 2.8–0.85 V (conversion reaction) and 0.85–0.01 V (alloying reaction), highly reversible conversion and alloying reactions in the $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ can be achieved separately.

5. APPLICATIONS IN SUPERCAPACITORS

Supercapacitors, also known as electrochemical capacitors, bridge the gap between conventional capacitors and rechargeable batteries. They have energy densities approaching those of conventional batteries, while their power density is generally 10 to 100 times greater. Additionally, they will tolerate many more charge and discharge cycles than batteries.

Bismuth chalcogenide manifests a rapid redox behavior that can be adapted for capacitor application. Bi_2X_3 compounds suffer from poor electron transfer rates, and thus their integration with capacitive materials [76] or conductive polymers [77] is a profitable strategy. These polymers are not only highly conductive but also electrochemically active, and their function in the capacitive composite is profound. A more promising agent is to use graphene, which is conductive, flexible, and chemically robust. Hybrids of Bi_2S_3 nanorods and graphene have been attempted by Nie *et al.* [78] and Vadivel *et al.* [79]. A high capacitance of 396 F g^{-1} at 1 A g^{-1} was reported for Bi_2S_3 -graphene hybrid electrode in a 2M KOH aqueous solution in the potential between -0.2 and 0.45 V (vs. SCE) [78]. Similarly, a capacitance of 290 F g^{-1} was obtained in the potential range between -1.0 and -0.2 V (vs. Ag/AgCl) [79].

In contrast to Bi_2S_3 and Bi_2Se_3 , Bi_2O_3 is frequently considered as a supercapacitor rather than battery material [80]. It can be used as anode for capacitors as it is electrochemically active in the potential range of -1.0 to -0.2 V vs. SCE [81]. The pseudocapacitive behavior of Bi_2O_3 was investigated by Gujar and coworkers ten years ago [82]. They demonstrated that the electrodeposited Bi_2O_3 film could afford a specific capacitance of 98 F g^{-1} in aqueous alkaline electrolyte within a potential window of 0.8 V . Charge storage mechanism involved the redox reaction between Bi_2O_3 to $\text{Bi}(\text{OH})^{2+}$. Later, several groups tried to enhance the capacitive property of Bi_2O_3 . [83-85] For instance, Yuan *et al.* incorporated nanoscale Bi_2O_3 into highly ordered mesoporous carbon (HOMC) [83]. A loading of 10% Bi_2O_3 in the hybrid materials resulted in an enhancement of 62% in the capacitance. The maximum value of capacitance reached 232 F g^{-1} at a sweep rate of 5 mV s^{-1} . This hybrid system took profit of ordered mesoporous structure, appropriately porous size of HOMC for quick ion diffusion and high specific surface area and large pseudocapacitance of Bi_2O_3 .

The capacitive property of Bi_2O_3 can be modulated by tailoring their morphology, shape, and size. Researchers have tried to design and prepare specific nanostructures to fulfill the requirement for rapid ion diffusion and fast charge transfer. Zheng *et al.* synthesized hierarchical rippled Bi_2O_3 nanobelts via an electro-deposition technique mediated by electrode potential oscillations [86]. When the potential periodically oscillated, hierarchical rippled nanobelts would be obtained. The rippled nanobelts exhibited a stable capacitance of 250 F g^{-1} at 100 mV s^{-1} , whereas the smooth sample only delivered a capacitance of 61 F g^{-1} .

Recently, flexible supercapacitors have captured much attention due to their potential as energy sources in stretchable and wearable electronics. Flexible Bi_2O_3 based supercapacitors have been developed [87, 88]. Graphene fiber-based supercapacitors have been assembled at the assistant of wet-spinning [87]. It is revealed that an increase of 60% in capacitance is obtained by incorporated only 1 wt% of Bi_2O_3 , and increased by 240% by addition of 3 wt% Bi_2O_3 (51 mF cm^{-2}). In another

case, Bi_2O_3 nanoparticles were hydrothermally grown on carbon nanofiber (CNF) paper, which is lightweight (1.6 mg cm^{-2}), porous, conductive, and flexible. A working electrode with a large areal mass of 9 mg cm^{-2} for Bi_2O_3 (~85 wt% of the entire electrode) was constructed. When the Bi_2O_3 anode was coupled with a MnO_2 cathode, flexible supercapacitors can be developed, as shown in Figure 9. This device had an operation voltage of 1.8 V, and could deliver a energy density of $43.4 \text{ } \mu\text{Wh cm}^{-2}$ (11.3 Wh kg^{-1} , based on the total electrode) and a maximum power density of 12.9 mW cm^{-2} (3370 W kg^{-1}). This work provides an example of large areal mass and flexible electrode for supercapacitors with high areal capacitance and high energy density, holding great promise for future flexible electronic devices.

6. APPLICATIONS IN OTHER ENERGY STORAGE

In recent, Bi and Bi_2X_3 have found application in aqueous rechargeable batteries (ARBs). In comparison to non-aqueous batteries, ARBs offer safer, cheaper and sustainable electrochemical energy technologies, but limited choices on reversible and stable aqueous redox systems remain a critical challenge. Two novel aqueous redox systems based on Bi [89] and Bi_2O_3 [90] have been recently enclosed into the portfolio, making the leap towards reliable and sustainable ARBs. Figure 10 gives an example of $\text{NiCo}_2\text{O}_4/\text{Bi}$ ARBs, where the single-crystalline 3D Bi architectures on flexible carbon cloth was used as anode, and NiCo_2O_4 nanowires as a cathode [89]. In 1 M KOH aqueous electrolyte, the Bi single electrode exhibited a capacity of 96.2 mAh g^{-1} at 4.5 A g^{-1} , retained 90.4 mAh g^{-1} at a much higher current of 45 A g^{-1} , and sustained 10 000 cycles without any capacity decay. In the cell scale, the flexible $\text{NiCo}_2\text{O}_4/\text{Bi}$ battery afforded a maximum energy density of 85.8 Wh kg^{-1} and a power density of 21 kW kg^{-1} , and the capacity retention over 1000 cycles is 89%. Such a superior electrochemical performance suggests that the $\text{NiCo}_2\text{O}_4/\text{Bi}$ aqueous rechargeable battery may find potential application in many vital fields.

Liu *et al.* reported a systematic research on a versatile Bi_2O_3 electrode, which was able to electrochemically store charges in numerous aqueous monovalent, divalent and trivalent metal ion electrolytes [90]. The Bi_2O_3 electrode demonstrated a high specific capacity ($\sim 357 \text{ mAh g}^{-1}$), outstanding rate capability (75 A g^{-1}) and good cycle life (4200 cycles) in a neutral mixed Li electrolyte. In a more interesting research, Chen *et al.* observed the storage of zero-valent atomic species (Cu, Sn, Ni, Co, etc.) in Bi_2Se_3 via a chemical reaction [91]. More crucially, the chemical route allows multiple atoms intercalation into the host lattice of Bi_2Se_3 , while the traditional electrochemical intercalation allows only a single atomic intercalant. This storage of multiple atoms in Bi_2Se_3 is of high reversibility, thus manifesting a novel research direction.

7. CONCLUSIONS AND PERSPECTIVES

Energy storage is playing a critical role in fostering the growth of the renewables and electric vehicles. Meeting the technique requirements represents a crucial challenge for current fuel cells, rechargeable batteries and supercapacitors. Owing to the unique structure and property, bismuth chalcogenides have shown to be of great promise to mitigate this challenge and potential to be utilized in various energy storage solutions such as H, Li, Na storage and supercapacitors.

Laminar Bi_2S_3 and Bi_2Se_3 have been well engineered for H adsorption, due to their structural voids for H accommodation. As for Li and Na storage, various bismuth materials show impressive electrochemical performance because chalcogenides can be reduced to metallic Bi and further react with Li or Na to give rise to alloys. Bi metal demonstrates favorable alloying capability with Li and Na, exhibiting a high theoretical level (385 mAh g^{-1} or 3800 mAh cm^{-3}). More importantly, alloying process occurs at a potential in the range of 0.5–0.8 V, which intrinsically eliminates the Li plating. Bi_2X_3 exhibits a higher capacity at the expense of reversibility, due to the difficulty of Bi oxidation by Li_2X and the possible dissolution loss of polychalcogenide species X_n^{2-} ($\text{X} = \text{S}$ and Se) in organic electrolytes. On the other hand, Bi_2S_3 and Bi_2O_3 have attracted much attention as anodes for supercapacitors, and have a potentiality for rechargeable aqueous batteries.

Researches on bismuth chalcogenides remain at the infant stage and significant challenges remain in terms of insufficient cyclability and rate capability. More efforts are urgently needed in this field. Further improvement in their electrochemical performance might rely on nanoengineering of porous structure, yolk-shell architectures, and surface and interfacial modification. The pores in bismuth materials provide sufficient sites and spaces for intercalant ions without structural rearrangement, thus boost the power and stability for H, Li, Na storage and supercapacitors. The yolk-shell architectures hold the intermediate polychalcogenides and acquire a better structural integrity, and therefore eventually achieve ultrastable cycling [92]. Moreover, elegant surface and interfacial modification via atomic layer deposition represents a powerful techniques for the rational design of material interfaces that dictate the kinetics of charge transfer in electrochemical devices [93-95]. This is effective and straightforward from the viewpoint of electrochemistry.

Application of diverse bismuth chalcogenides in various electrochemical systems has proven to be an intriguing and profitable research field. Further efforts are needed to fully investigate the design, preparation, structure and properties of bismuth materials. In particular, deep understanding of the Li_3Bi and Na_3Bi alloying mechanism and the nature of charge transfer upon the alloying process is required. Such understanding could lead to the discovery of novel energy storage systems not present previously and revolutionize the way through which the electrodes are engineered and devices constructed. Success of this research relies on advancement of in situ analytical techniques

and the accurate monitoring of the reaction process. It is optimistic to believe that the bismuth materials have hitherto been applied in many more energy systems and will play a more fundamental role in the future.

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Figures

Figure 1. Bismuth (Bi) in the periodic table and elemental bismuth metal.

Figure 2. Structure projection from b-axis direction of the typical polymorphs of (a) monoclinic Bi_2O_3 , (b) orthorhombic Bi_2S_3 , and (c) rhombohedral Bi_2Se_3 . The cations are colored purple with the anions red. The

Figure 3. Hydrogen storage in disc-like Bi_2S_3 nanofabrics. (a) Charge–discharge curves of disc-like Bi_2S_3 nanofabrics at a rate of 50 mA g^{-1} . (b) Cyclic voltammograms of Bi_2S_3 nanofabrics and nanorod bundle electrodes at a scan rate of 50 mV s^{-1} . Reproduced with permission [27]. Copyright 2008, Wiley-VCH.

Figure 4. Schematics illustrate how an ion conductive matrix (e.g. Li_3PO_4) helps to realize a long Li cycling in Bi anodes. (a) Bi particle pulverizes upon Li cycling, resulting in loss of electrical percolation and thus capacity. (b) An ion conductive matrix (e.g. Li_3PO_4) ionically connected Bi particles to maintain conductivity.

Figure 5. Schematic illustrating the two-step reaction of bismuth chalcogenide Bi_2X_3 with Li. Bi_2X_3 is first reduced to Li_2X_3 and Bi (I), which then alloys with Li to give rise to Li_3Bi (II). The first step is generally less reversible than the second one.

Figure 6. SEM images of $\text{Bi}_2\text{S}_3@\text{CNT}$ hybrid before (a, b) and after (c) heating at 200 °C for 2 hours. (d) TEM image of final $\text{Bi}_2\text{S}_3@\text{CNT}$ hybrid. (e) Rate cycling behavior and (f) cyclic voltammograms of the $\text{Bi}_2\text{S}_3@\text{CNT}$ measured at various rates. Reproduced with permission [50]. Copyright 2014, Wiley-VCH.

Figure 7. Illustration of the different structural and electrochemical pathways in the Na–Bi system. Reproduced with permission [68]. Copyright 2016, American Chemical Society.

Figure 8. Na storage in Bi_{0.94}Sb_{1.06}S₃ nanorods. (a) Cycle performance of Bi_{0.94}Sb_{1.06}S₃-graphite, Sb₂S₃-graphite, and Bi₂S₃-graphite electrodes at a current density of 1 A g⁻¹ and in the voltage range of 0.01–2.80 V in sodium-ion batteries. (b) Capacity retention of the electrodes in sodium-ion batteries after 120 and 200 cycles. (c, d) Rate capabilities and potential profiles of Bi_{0.94}Sb_{1.06}S₃-graphite electrode at various current densities in sodium-ion battery. Reproduced with permission [75]. Copyright 2015, American Chemical Society.

Figure 9. (a) Schematic illustration of the structure of the as-assembled flexible supercapacitor. The two digital images show the flexibility. (b) Comparison of CV curves collected for Bi_2O_3 and MnO_2 electrodes at a scan rate of 50 mV s^{-1} . (c) CV curves of the flexible supercapacitor at different scan rates. (d) Galvanostatic curves at various current densities. (e) Areal and specific capacitance as a function of current density. (f) Cycling performance of the supercapacitor at 6 mA cm^{-2} over 4000 cycles. Reproduced with permission [88]. Copyright 2015, Wiley-VCH.

Figure 10. (a) Schematic diagram of the NiCo₂O₄//Bi battery. (b) CV curves of the NiCo₂O₄//Bi battery at various scan rates. (c) Galvanostatic discharge profiles of the NiCo₂O₄//Bi battery at different current densities. (d) Nyquist plots of the NiCo₂O₄//Bi battery. (e) Cycling performance of the NiCo₂O₄//Bi battery collected at a current density of 4 A g⁻¹ for 1000 cycles. The inset is the 1st and 1000th discharge curves collected for the NiCo₂O₄//Bi battery. (f) Specific capacity of the NiCo₂O₄//Bi battery as a function of bending time. The inset is a digital photo of the NiCo₂O₄//Bi battery under normal and bending conditions. Reproduced with permission [89]. Copyright 2016, Wiley-VCH.