Polyaniline-based Electrodes: Recent Application in Supercapacitors and Next Generation Rechargeable Batteries

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This review highlights the versatility of polyaniline (PANI) for application in the electrodes of energy storage devices — supercapacitors and next-generation batteries (sodium-ion - SIB and lithium-sulfur - LiS). Supercapacitor electrodes with high energy storage capability and cycle life have been developed based on both neat PANI as well as its composites with carbon or inorganic pseudocapacitors. In batteries, tailorable synthesis of PANI to confine/coat nanostructures of electroactive materials (Na^+ host materials in SIBs or sulfur in LiS) has resulted in notable improvement in utilization, stability and durability of these materials due to PANI's high conductivity, specific material interaction and its ability to ameliorate stress on the nanostructures caused by large volume changes during cycling. Limitations of PANI in such electrodes are discussed and possible future directions have been proposed.

Introduction

Quest for green energy, depleting energy reserves and the ever increasing energy demand for applications such as portable electronics, electrified transportation and grid-level energy storage have accelerated research in sustainable energy alternatives.[1] For the last two decades, lithium ion batteries (LIBs) have transformed the portable electronics industry owing to their high energy density and long life cycle. However, new market demand for sustainable higher energy and power sources calls for the development of new generation of LIBs or alternative energy storage devices. Rechargeable batteries such as lithium-air, lithium-sulfur (LiS), sodium-ion (SIB), and supercapacitors have received intense interest recently as energy storage prospects. The appeal for these energy devices lies in the natural abundance of their electrode materials, benign environmental impact, well-understood electrochemistry and promising energy storage capability.

Although important developments have been made on electrodes for supercapacitors and rechargeable batteries in recent literature, significant challenges related to electrochemical performance/utilization and durability remain.[2,3] The low electrochemical utilization is attributed to electrode morphology (small accessible surface area) and inadequate conductivity whereas the poor durability is related to electrode structural instability and/or loss of active materials during cycling. Therefore, there has been plenty of research focused on studying new electrode materials, nanocomposites and architectures in an attempt to address the aforementioned performance deficiencies. Polyaniline (PANI) is a readily available p-type conducting polymer which has commanded considerable attention for application in electrodes of most energy devices either as a sole electrode active material or as a supplement material to

enhance performance. PANI is commonly synthesized through chemical oxidative polymerization of aniline using a strong oxidant. Electrochemical synthesis of polyaniline has also been widely applied. PANI can exist in three different oxidation states: leucoemeraldine, emeraldine base is the partially-oxidized and pernigraniline which are the fully reduced, partially oxidized and fully oxidized states, respectively.[4] Synthesis of PANI is largely carried out in acidic conditions, which result in a protonated/doped emeraldine salt. External doping or de-doping of the emeraldine salt has also been achieved using an acid or base, respectively.[5] Conductivity of PANI is strongly dependent on the degree of oxidation and the doping. Doped emeraldine base is the most conductive state, with conductivity ranging from 0.1 to over 100 S/cm.[6] Un-doped emeraldine and the fully reduced/oxidized states show conductivity in the order of 10^{-10} S/cm. PANI nanostructures are prepared either via a template-assisted method where an external soluble or insoluble substrate with pre-formed nanoscale features such as a metal oxide is employed or template-free technique where material's ability to self-assemble into various morphologies depending on the synthesis conditions (pH, temperature, nature of dopants, etc.), is exploited. [7] [8].

This short review will provide a synopsis of recent research in the application of PANI and its nanocomposites in electrodes for supercapacitors and new generation rechargeable batteries. Focus will be placed on highlighting how PANI properties such as easy and flexible synthesis process, unique chemistry/redox process, mechanical flexibility and high electrical conductivity contribute to the high, reversible capacity and long term stability of electrodes for supercapacitors, SIBs and LiS batteries. We will also discuss the limitations of PANI application in such electrodes and possible future directions will be proposed.

PANI in supercapacitors

PANI is the most studied member of the conducting polymer family for supercapacitor application due to its excellent electrical conductivity, high theoretical pseudocapacitance (750 F g^{-1})[9] derived from its reversible redox reactions and easy synthesis. However, although its application in supercapacitor electrodes has shown tremendous promise thus far, some lingering shortcomings prevent the realization of its optimal performance. These limitations include: (a) low capacitance retention at high charge/discharge rates and (b) poor durability after long term cycling (usually after ~ 1000 cycles).[10-12] The latter is caused by structural deterioration of PANI due to large volume changes associated with repeated doping and de-doping and over-oxidation of the polymer at high potential.[13] The former limitation is caused by the morphology, which affects electrolyte penetration and hence ion transfer, and electrical conductivity of the PANI electrodes. This is in addition to the transport limitations at the polymer-electrolyte and electrode-current collector interfaces. In this section, we will examine the research effort within the last three years to address these PANI shortcomings. These efforts have included improvement of PANI electrode architectures, development of PANI composites and adoption of redox active electrolytes.

PANI-based Composites as Supercapacitor Cathodes

Bulk of the PANI supercapacitor research so far has focused on nanocomposites of PANI with carbon and/or inorganic compounds to reinforce its electrical conductivity and/or mechanical stability to improve rate capability and cycle life performance. PANI/carbon composites have particularly been extensively studied since carbon is a readily available material with excellent electrical conductivity and mechanical properties.[14] A synergistic combination of excellent electrical conductivity, high surface area/pore volume and mechanical resilience of carbonaceous backbone and high pseudocapacitance of PANI is realized in such hybrid electrodes.[15] **Of the carbon family, graphene has attracted notable attention as a viable host/substrate material for PANI. Graphene possesses large theoretical surface area ($\sim 2600 \text{ m}^2/\text{g}$), superior chemical/mechanical stability, good processability and potential for scalability. Moreover, graphene is considered one of the best candidates for flexible electrode materials. [16] The resultant graphene/PANI nanocomposite electrodes have demonstrated high capacitance, long cycle life and impressive flexibility in supercapacitors. [17] The synthesis and application of graphene/PANI nanocomposites, has been comprehensively reviewed recently and the reader is directed to these reviews for detailed information.[18,19] Recently, our lab developed binder-free freestanding PANI-coated porous carbon nanofiber electrodes which achieved SC of 409 F g^{-1} at 0.1 A g^{-1} , 80% of which was retained at a high current density of 10 A g^{-1} . [20] Control experiments using PANI-coated, non-porous carbon nanofibers delivered much lower SC at the same current densities indicating that the double layer capacitance of the underlying carbon was retained and true integration of double layer and pseudocapacitance was achieved. Overall, the PANI/carbon composite electrodes have demonstrated good initial specific capacitance (SC) and reasonable capacitance retention ($>80\%$) after long cycling (1000-5000 cycles) as illustrated in table 1.[21-23]. Fabrication and application of PANI/carbon electrodes, however, often face challenges such as complex procedure for preparation of hierarchical carbons, low loading of deposited PANI and low capacitance contribution of the carbon backbone (if any).[24,25]**

Composites of PANI with transition metal oxides have also been studied owing to the inherently high pseudocapacitance of these materials.[26] MnO_2 is considered as one of the promising members of the metal oxide group for supercapacitor applications due to its low cost and eco-friendliness in addition to excellent theoretical pseudocapacitance (1370 F g^{-1}). [27] Its composite with PANI has shown promising electroactivity where PANI acts not only as nanostructured scaffold for MnO_2 but also as a conductive medium. Composites of PANI with other transition metal oxides such as nanostructured V_2O_5 , TiO_2 , RuO_2 and hollow MoO_3 (h- MoO_3) have also been investigated with good reported electrochemical performance.[28-30] Unfortunately, high cost, low conductivity and environmental unfriendliness of some of these oxides hinder the development of their composites with PANI.

Pure PANI Cathodes

Supercapacitor cathodes based on neat PANI (without use of additives) can potentially provide high electrode-level specific energy density. To offset PANI's mechanical instability and to maximize its utilization, interesting PANI architectures based on 1-D and 3-D interconnected nanostructures have been developed and studied for supercapacitors applications.[31,32] The nanostructured morphology is imperative since most of the PANI redox reactions occur at or

near the electrode/electrolyte interface. The nanostructures help to truncate charge transfer pathways, relief strains within the electrode due to electroactivity and in some cases, enable new reactions not possible within bulk materials. [33] Synthesis techniques and application of various 1-D PANI nanomaterials have been studied for several years now. Recently hollow nanofibers synthesized via template technique [10] and nanotubes prepared via template-less process (self-assembly) [34] delivered high SCs of 601 F g^{-1} and 625 F g^{-1} , respectively. The excellence in electroactivity of these 1-D nanostructures emanate from their morphology marked by high aspect ratio, porous surface and/or tubular morphology, which enables good electrode/electrolyte interaction, leading to efficient charge transfer to the reaction interface. Unfortunately, most of the supercapacitor electrodes based on 1-D PANI nanostructures still display undesirable loss in capacitance as shown in table 1 below. In comparison, recent works based on porous 3-D interconnected PANI nanostructures have shown promising capacitance retention capability at both higher current densities and after over 1000 cycles. Such improvement stems from the 3-D intertwined nanostructured network, which enables continuous electron conductivity as well as enhanced mechanical stability, and the hierarchical porosity, which facilitates faster ion diffusion/higher rate capability. Moreover, the macropores within such 3-D structures possibly relieve the stresses associated with volume changes during the doping/de-doping of PANI leading to enhanced cycling stability. Recently novel synthetic method was adopted where dopants acts as crosslinkers to synthesis conducting polymer gels (CPGs).[35] Crosslinked 3-D PANI hydrogel fabricated using phytic acid as both a gelator and a dopant showed excellent electron conductivity of 0.11 S/cm and high capacitance retention of 93% at 5 A g^{-1} with 83% capacitance retention after 10000 cycles.[36] Similarly, a robust 3-D crosslinked PANI (see figure 2) electrode developed via concurrent inorganic (HCl) and organic acid (Phytic acid, PA) doping of PANI during the self-assembly process delivered a SC of 350 F g^{-1} which was found to be stable over a current density range of 1 to 40 A g^{-1} . [37]

Redox-active Electrolytes for PANI Supercapacitors

An alternative route for the enhancement of PANI-based electrode pseudocapacitance and durability has been shown recently via modification of the conventional electrolytes using redox active agents such as hydroquinone.[38] The redox active species provide additional Faradaic reactions and can increase electrolyte conductivity and decrease charge transfer resistance leading to improved pseudocapacitance and durability. Vonlanthen and co-workers designed a supercapacitor consisting of symmetric PANI electrodes and $1\text{M H}_2\text{SO}_4$ electrolyte modified with benzoquinone-hydroquinone (HQ-BQ) mediators.[39] A SC of 524 F g^{-1} and unprecedented capacitance retention over 50000 cycles was reported. In comparison, PANI tested with no redox species showed a SC of 418 F g^{-1} and a 20% loss in capacitance after 2800 cycles.

Table 1. Polyaniline-based supercapacitors — Fabrication techniques, electroactivity (per gram of total electrode) at low and high current densities (CD), and cycle life.

	Low CD rate SC in F g^{-1} (Current Density)	High CD rate SC in F g^{-1} (Current Density)	% Retention (# cycles)
PANI hybrids	PANI wt%		

Graphene, [22]	40	448 (1 A g ⁻¹)	334 (10 A g ⁻¹)	81 (5000)
CNFs, [20]	48	409 (0.1 A g ⁻¹)	327 (10 A g ⁻¹)	80 (1000)
MWCNTs, [40]	95	530 (1 A g ⁻¹)	500 (3 A g ⁻¹)	90 (1000)
MnO ₂ , [41]	90	525 (2 A g ⁻¹)	330 (10 A g ⁻¹)	77 (1000)
V ₂ O ₅ , [28]	50*	443 (0.5 mA cm ⁻²)	281 (5 mA cm ⁻¹)	92 (5000)
Pure PANI Morphology	Synthesis Method			
Nanotubes ^(a) , [34]	self-assembly	625 (1 A g ⁻¹)	481 (10 A g ⁻¹)	77 (500)
Nanofiber ^(a) , [42]	template, MnO ₂	404 (1 A g ⁻¹)	385 (10 A g ⁻¹)	61 (5000)
Nanorods ^(a) , [32]	self-assembly	455 (1 mV s ⁻¹)	—	65 (1300)
Hydrogel ^(b) , [36]	soft template	450 (0.5 A g ⁻¹)	420 (5 A g ⁻¹)	83 (10 000)
CPANI ^(b) , [37]	self-assembly	350 (1 A g ⁻¹)	315 (40 A g ⁻¹)	99 (500)
CPANI ^(b) , [43]	Self-assembly	274 (1 A g ⁻¹)	—	89 (1300)
Redox-Electrolyte				
H ₂ SO ₄ +HQ-BQ, [39]		524 (12.5 mA cm ⁻²)	—	>99.5(50000)
H ₂ SO ₄ + HQ, [44]		584 (1 A g ⁻¹)	—	68 (5000)

^a1-D nanostructures, ^b 3-D nanostructures, CPANI—crosslinked PANI chains. * Calculated from data provided.

Lithium-Ion batteries

Demand for high energy and power density energy devices for large scale application such as grid-level energy storage and transportation calls for development of next generation lithium ion batteries and/or beyond lithium ion batteries. The state of the art lithium-ion batteries face challenges such as poor safety, high production cost and limited energy density of the electrode materials (the practical capacity of graphite is ~300 mAhg⁻¹ while that of the LiCoO₂ is ~140 mAhg⁻¹).[45] Nanostructured inorganic electrode materials such as copper vanadates/oxides, silicon, MoS₂, and LiVPO₄ with high energy storage capability are being explored for next-generation Li-ion batteries.[46-48] However, their performance is hampered by poor electrical conductivities and short lifespan.[49] The poor cyclability is attributed to large volumetric changes due to intercalation/de-intercalation of Li ions, which lead to distortion of the inorganic nanomaterial morphology. Hierarchical PANI/inorganic nanocomposite has proven to be one plausible solution to address these deficiencies.[50-52] PANI (used in both the anode and cathode of Li-ion) enhances the electrical conductivity and provides buffer to accommodate volumetric expansion of the aforementioned inorganic materials. Sengodu *et al* recently reviewed the application of conducting polymers in Li-ion batteries and the reader is directed to this review article for the role of PANI in next generation Li-ion batteries. [53]

Beyond lithium ion batteries: Role of PANI

Sodium ions batteries (SIBs)

Sodium is an abundant and low cost element with similar physical and chemical characteristics as Li.[54] Although SIBs possess lower gravimetric capacity compared to LIBs (1169 mAhg⁻¹ for Na vs. 3829 mAhg⁻¹ for Li), SIBs are considered suitable alternatives to LIBs on the basis of cost, safety and sustainability. SIBs rely on cation intercalation/de-intercalation mechanisms

similar to those of LIBs. The progress of SIBs, however, has been thwarted by lack of appropriate active materials for both anode and cathode. Na^+ is ~40% larger in diameter than Li^+ , which makes it difficult to find a host material with sufficiently large interstitial spacing to host Na^+ and allow reversible insertion/extraction process.[55] Hard carbon, inorganic compounds such as transition metal oxides and redox organic materials have been studied for SIB electrodes.[56-58] These electrode materials have been extensively reviewed elsewhere.[59,60] The extent of discussion in this section will look into recent studies involving application of PANI in SIB electrodes either as auxiliary material to promote electroactivity of the aforementioned electrode materials or as a potential independent electrode host material for Na ions.

SIB Anode

PANI has been utilized in SIB anodes as a supplementary material to promote electrical conductivity and structural stability of inorganic compounds such as tin dioxide and cobalt sulfide. These inorganic compounds are promising anode materials for Na-ion batteries due to their low cost, minimal environmental pollution and high theoretical capacity.[61] However, their application is jeopardized by poor cycle life caused by large volume expansion during insertion and extraction of the large Na^+ and low electrical conductivity. The repeated volume changes during cycling cause degradation of nanostructures and agglomeration of nanoparticles thus impeding electrolyte penetration and ion transport. Core-shell nanostructures of SnO_2 hollow sphere-polyaniline composite ($\text{SnO}_2\text{-HS@PANI}$) [62] delivered reversible capacity of 213.5 mAhg^{-1} after 400 cycles at 300 mA g^{-1} while the PANI-free SnO_2 hollow spheres ($\text{SnO}_2\text{-HS}$) and bare SnO_2 particle anodes retained only 145 and 14.4 mAhg^{-1} , respectively, after 400 cycles at the same current density. The $\text{SnO}_2\text{@PANI}$ nanocomposite also exhibited higher capacity retention compared to $\text{SnO}_2\text{@carbon nanotubes}$ and $\text{SnO}_2\text{/reduced graphene}$. [61,63] Similar improvement in performance was observed for $\text{Co}_3\text{S}_4\text{@PANI}$ nanotube composites (see figure 3), [64] which exhibited a capacity retention of 252.5 mAhg^{-1} and 170.1 mAhg^{-1} at high current rate of 4000 mA g^{-1} after 100 and 400 cycles, respectively. In comparison, the bare Co_3S_4 anode only retained 58.2 mAhg^{-1} after 100 cycles.

SIB Cathode

PANI is favorable as an active SIB cathode material over inorganic compounds on the basis of availability and flexibility of its framework (for rapid sodiation and de-sodiation). Its application, however, is limited by low doping/de-doping level and lack of Na storage capability, especially for the case of Na deficient anode. Na-rich PANI cathode, poly(aniline-co-aminobenzenesulfonic sodium) (PANS), was recently developed by grafting electron withdrawing $-\text{SO}_3\text{Na}$ groups on PANI chains and investigated for SIB application.[65] By grafting sulfonic groups on PANI chains, Na^+ can be inserted and extracted from the polymer chain during charge and discharge, respectively, therefore changing the mechanism of operation from the convectional doping/de-doping to insertion/extraction. The self-doping, PANS cathode delivered a reversible capacity of 133 mAh g^{-1} with an excellent capacity retention of ~97% after 200 cycles. The PANS cathode also showed an impressive rate capability possibly due to the flexible polymer framework, which offers less resistance to insertion/extraction of Na^+ . Electron withdrawing o-nitroaniline has also

been grafted onto PANI chains and tested as a cathode for SIBs.[66] The aniline-nitroaniline copolymer delivered a capacity of 180 mAhg^{-1} at an average potential of 3.2 vs Na/Na^+ and a reversible capacity of 173 mAhg^{-1} after 50 cycles.

Lithium sulfur batteries

Lithium-Sulfur (LiS) batteries are attractive energy storage devices for large scale applications due to the natural abundance of sulfur and its high theoretical energy density (2600 vs. $\sim 400 \text{ Whkg}^{-1}$ for Li-ion).[67] In LiS batteries, lithium is oxidized at the anode while sulfur is reduced at the cathode through a series of reactions with Li^+ to form Li_2S . Commercialization of LiS, however, has been hampered by low sulfur utilization and poor cycle life. [68] While the low sulfur utilization is a results of its insulating nature, the low battery cyclability is caused by the dissolution and shuttling of the intermediate lithium polysulfides (Li_2S_n , $2 < n < 8$) and volumetric changes during cycling [69]. Sulfur composites with various carbon materials and conducting polymers have been developed to address these challenges by promoting electrical conductivity and encapsulating sulfur and hence the polysulfides. Carbon/sulfur composites have been well studied and their advantages/limitations delineated.[68,70] PANI has been favorably studied for application in LiS cathodes due its processability at room temperature, strong affinity for the intermediate polysulfide and flexible framework which allows for sulfur volumetric expansion observed during life cycle performance tests.

The positive charges induced on PANI amino groups during acid doping promote electrostatic interaction between the polymer and the negatively-charged polysulfides (S_n^{2-}) during the charge-discharge process. Such interactions possibly result in chemical immobilization of the polysulfides, thereby limiting dissolution and migration of these intermediate species away from the cathode. Gao and co-workers prepared ultrathin sulfur-wrapped PANI nanofibers with core-shell morphology via heterogonous nucleation of sulfur on water dispersed PANI nanofibers.[71] The PANI@sulfur nanofiber cathodes showed an initial discharge capacity of 977 mAh g^{-1} with over 83% retention after 100 cycles at 1C and excellent rate capability up to 3C.

To more effectively impede dissolution of polysulfides and to also accommodate volume changes, several works have incorporated a heating (vulcanization) step during the fabrication of PANI/sulfur nanocomposites with tubular, hollow-spherical and yolk-shell morphologies.[72-74] The heat treatment process results in a small amount of S reacting with the polymer backbone giving rise to a 3-D, crosslinked sulfur-polymer backbone with the inter- and intra-chain disulfide bonds interconnected via vulcanization.[73] The unreacted S and polysulfides are physically and chemically trapped within the polymer molecular framework. Furthermore, the void spaces created due to the polymer-sulfur reaction provide breathing room to accommodate volume changes associated with Li/S electrochemistry. Hollow sulfur@PANI spheres recently demonstrated a reversible discharge capacity of 602 mAhg^{-1} after 1000 cycles at 0.5C.[72]

Several recent works have developed and investigated layered ternary composites of PANI/sulfur/carbon as LiS cathodes with the aim to combine the high mechanical strength and electrical conductivity of carbon with the enhanced sulfur confinement by PANI. Two

fabrication methods have been adapted for such ternary composites based on the sequence of sulfur or PANI deposition on the carbon substrate. The first approach involves the deposition of sulfur on a high surface area carbon nanomaterial and coating of the resultant bilayer system with a thin layer of PANI to encapsulate sulfur and prevent out-diffusion of the polysulfides. This approach was shown by Kim *et al* who developed a freestanding PANI/sulfur/single wall carbon nanotube (PANI/S/SWNT) film as illustrated in figure 4.[75] The composite cathode showed initial discharge specific capacity of 1415 mAhg^{-1} with retention of 1011 mAhg^{-1} after 100 cycles at 0.2C. The second approach entails polymerizing a thin layer of PANI on the surface/pores of a carbon material followed by deposition of sulfur. The PANI layer is intended to foster chemical interaction between sulfur and the underlying high surface area carbon. LiS cathodes based on sulfur/PANI/mesoporous carbon reported the highest discharge capacity of 675 mAhg^{-1} after 200 cycles at 0.1 C.[76] PANI provided a soft padding between carbon and sulfur, reducing detachment of sulfur and lithium polysulfide within the meso-pores of the carbon material during cycling.

Ultrathin composite film of PANI/MWCTs has also been recently developed to serve as an interlayer between the separator and the LiS cathode. Chang *et al* [77] functionalized one side of the separator facing the cathode with ultralow loading of 0.01 mg cm^{-2} of PANI nanofibers and multiwalled carbon nanotubes (PANiNFs/MWCNT) and investigated its performance in LiS batteries. The interlayer facilitated reversible capacities of 709, 641 and 612 mAhg^{-1} , respectively, at C/5, C/2 and 1C after 100 cycles. The higher utilization of sulfur was attributed to the additional electron pathway provided by the PANI-based coating ensuring accessibility of the active material. The enhanced cyclability was due to the PANiNF/MWCNT filter blocking the polysulfides via chemical interaction with the PANI imine groups as well as via reactivation of the trapped species by the conductive separator.

Summary and perspective

This review provides a brief overview of the present status of the application of PANI and its composites in the electrodes of supercapacitors, sodium-ion and lithium-sulfur batteries. Although satisfactory research progress has been realized both in supercapacitors and the covered rechargeable batteries, much fundamental studies and electrode fabrication techniques remains to be done. One of the areas that can be further improved in the fabrication of electrodes is the development of binder-free and freestanding electrodes. Few freestanding film electrodes based on PANI hybrids have been reported with good electrochemical performance.[16,20] However, most electrodes in the literature are prepared by making a paste consisting of the active materials, binders and conductive materials, which is then coated on a current collector. Such rigorous process is likely to cause impairment to the fabricated PANI-based nanostructures. The continuity of electron transport pathways and/or extent of encapsulation/coating of active materials for the battery configurations will most likely be interrupted. Furthermore, by incorporation of binders, additional dead weight is introduced to the system. The long-term stability of PANI-based electrodes needs to be enhanced for commercialization of these energy devices (particularly supercapacitors). In light of recent impressive electroactivity and stability of PANI-based electrodes demonstrated in redox-active electrolytes where capacitance retention

was observed over 50k cycles [39], further research on nanostructured PANI/PANI hybrid electrode in such and other electrolyte systems [78] might prove invaluable in enhancing electrode stability.

There is a need for fundamental *in situ* studies on aspects such as PANI redox state, conductivity, structural integrity and chemical interaction of PANI with active material and/or unstable intermediate species during battery cycling, where PANI is largely added for either electrical conductivity and/or interaction with active species. The redox state of PANI, and consequently its conductivity, is highly dependent on electrode potential. Emeraldine is the most conductive state and hence the most appropriate state for electrode application where high electron conductivity is paramount. It will be therefore insightful to study the extent of PANI redox process, if any, and its reversibility during charge-discharge process since such process might impact negatively on electrode electroactivity/stability. Moreover, it will be invaluable to decipher the extent of chemical interaction between PANI and sulfur/intermediate polysulfide and effect of ions consumptions to such interaction during charge-discharge process for the case of LiS batteries.

There has also been some oversight in application of PANI in LiS electrodes — electrode fabrication processes such as heat treatment (vulcanization process) is likely to cause degradation of dopants and therefore diminish PANI conductivity significantly. Most literature works have also not studied the capacity arising from the cation doping/de-doping of PANI chains in battery electrodes that may have resulted in overestimation of the capacity of the active material(s).

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Figures

Figure 1: Schematic showing the versatility of polyaniline for application in energy storage devices both as an active material and as a support material to enhance device capacity and/or stability.

Figure 2: PANI application in supercapacitors: TEM images showing PANI doped by HCl (a), phytic acid (b) and crosslinked PANI obtained by concurrent-doping with HCl/phytic acid (c). Rate capability (d) and life cycle (e) for PANI electrodes obtained by doping PANI with different HCl/Phytic acid ratios. Best performance was obtained for co-doped PANI sample with 45% phytic acid (PANI 45PA) which showed unprecedented rate capability upto 40 A/g. Reprinted with permission from Gawli Y, Banerjee A, Dhakras D, Deo M, Bulani D, Wadgaonkar P, Shelke M, Ogale S: **3D Polyaniline Architecture by Concurrent Inorganic and Organic Acid Doping for Superior and Robust High Rate Supercapacitor Performance**. Copyright 2016 Nature Publishing Group.

Figure 3: PANI application in sodium-ion batteries: TEM images of bare Co_3S_4 nanotubes (a), PANI coated Co_3S_4 nanotubes ($\text{Co}_3\text{S}_4 @ \text{PANI}$) (b), and $\text{Co}_3\text{S}_4 @ \text{PANI}$ at higher magnification (c) and electrochemical performance (d) of PANI (green), Co_3S_4 nanotubes (blue) and $\text{Co}_3\text{S}_4 @ \text{PANI}$ nanotubes. Coating of Co_3S_4 nanotubes with PANI is seen to enhance life cycle performance. Reprinted with permission from Zhou Q, Liu L, Huang Z, Yi L, Wang X, Cao G: **$\text{Co}_3\text{S}_4 @ \text{polyaniline}$ nanotubes as high-performance anode materials for sodium ion batteries.** Images adapted with permission of The Royal Society of Chemistry.

Figure 4: PANI application in Lithium-sulfur batteries: SEM images of freestanding SWNTs (a), sulfur deposited on SWNTs, S/SWNT (b), PANI polymerized on S/SWNT to encapsulate sulfur and trap polysulfides, PANI-S/SWNT (c) and life cycle performance (d) of S/SWNT (black) and PANI-S/SWNT (red). PANI coated S/SWNT shows better capacity retention and coulombic efficiency after 100 cycles. Reprinted with permission from Kim JH, Fu K, Choi J, Kil K, Kim J, Han X, Hu L, Paik U: **Encapsulation of S/SWNT with PANI web for enhanced rate and cycle performance in lithium sulfur batteries**. Copyright 2015 Nature Publishing Group.