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Investigating the Complex Chemistry of Functional Energy Storage Systems: The Need for an Integrative, Multiscale (Molecular to Mesoscale) Perspective

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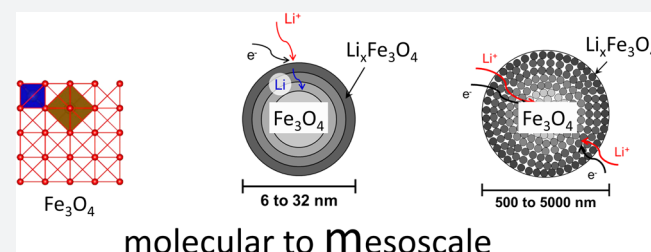
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ABSTRACT: Electric energy storage systems such as batteries can significantly impact society in a variety of ways, including facilitating the widespread deployment of portable electronic devices, enabling the use of renewable energy generation for local off grid situations and providing the basis of highly efficient power grids integrated with energy production, large stationary batteries, and the excess capacity from electric vehicles. A critical challenge for electric energy storage is understanding the basic science associated with the gap between the usable output of energy storage systems and their theoretical energy contents. The goal of overcoming this inefficiency is to achieve more useful work (w) and minimize the generation of waste heat (q). Minimization of inefficiency can be approached at the macro level, where bulk parameters are identified and manipulated, with optimization as an ultimate goal. However, such a strategy may not provide insight toward the complexities of electric energy storage, especially the inherent heterogeneity of ion and electron flux contributing to the local resistances at numerous interfaces found at several scale lengths within a battery. Thus, the ability to predict and ultimately tune these complex systems to specific applications, both current and future, demands not just parametrization at the bulk scale but rather specific experimentation and understanding over multiple length scales within the same battery system, from the molecular scale to the mesoscale. Herein, we provide a case study examining the insights and implications from multiscale investigations of a prospective battery material, Fe_3O_4 .



molecular to mesoscale

INTRODUCTION

Batteries are application driven, scientifically complex electrical energy storage (EES) systems used for portable devices, electric transportation, and stationary electrical storage at power generation plants. High energy density batteries, such as lithium ion, dominate the portable electronics markets where the devices and the batteries are typically hand-held and small. Widespread implementation of large format batteries such as those used for electric vehicles or for stationary electrical storage demands additional consideration of factors contributing to inefficiency of the EES leading to heat generation. While the generation of heat by a small battery may be an undesirable nuisance, the generation of heat by a large battery demands careful management of the generated heat to avoid compromise of performance or possible safety issues.

This leads one to consider the governing principle of all EES systems that energy is the sum of work and heat, eq 1. The goal for EES is to maximize useful work (w) and minimize waste heat (q), Figure 1.

$$\Delta E = q + w \quad (1)$$

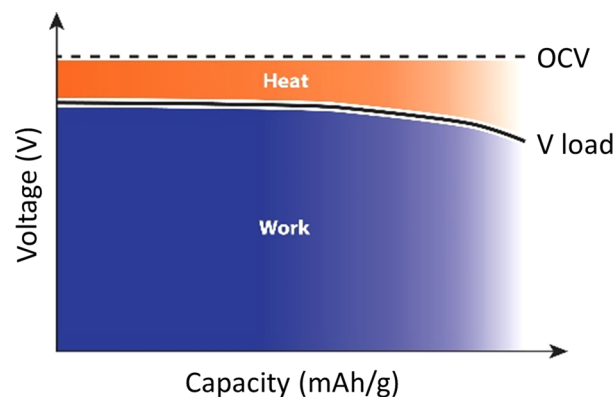


Figure 1. Delivered work (purple) and heat (orange).

When a battery operates, ions and electrons are transported over multiple size domains. Over time, resistance caused by

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phase changes in the solids and changes in the composition and structure of the interfaces can evolve, leading to inefficiency. In battery terms, inefficiency can be described by polarization where the difference between the theoretical potential and usable output is described by eq 2, where E is the operating potential, E° is the standard potential, i is the operating current, R_i is the internal resistance of the cell, $(\eta_{ct})_a$ and $(\eta_{ct})_c$ represent activation polarization, and $(\eta_c)_a$ and $(\eta_c)_c$ represent concentration polarization at the anode and cathode, respectively.

$$E = E^\circ - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i \quad (2)$$

Notably, E° does not accurately reflect E without considering the factors which are dictated by transport phenomena. For example, activation and concentration polarization describe kinetics of charge transfer and mass transfer and internal resistance reflects the conduction properties of the constituent materials and their interfaces. Often bulk methods of analysis cannot robustly describe the heterogeneity of ion and electron flux causing localized resistance within an electrode and at the interfaces. In a similar fashion, local methods in isolation cannot fully represent the complexity of the full working system. In other words, macroscopic phenomena should be interpreted based on information elicited at the atomic, interfacial, and mesoscale levels. Therefore, to predict and ultimately control EES systems, inefficiencies must be addressed not just as a bulk property (heat), but rather as localized resistance at the molecular to mesoscale levels.

Consideration of battery inefficiency then leads to a fundamental issue in battery science: the discrepancy between the theoretical and usable energy content of a battery. While theoretical energy estimates, including theoretical capacity, voltage, and energy density, are often provided in the literature for Li ion battery systems and components, chemical changes upon charge and discharge can have significant impact and limit their utility as a robust tool to analyze a potential material's efficiency and properties under working conditions. The ability to identify the factors that contribute to performance differences between theoretical versus functional capacity, voltage, and energy density as well as understanding the mechanism of discharge will lead to a comprehensive understanding of an EES system,¹ enabling pointed and efficient design of future batteries.

While the generation of heat by a small battery may be an undesirable nuisance, the generation of heat by a large battery demands careful management of the generated heat to avoid compromise of performance or possible safety issues.

One approach to analyze multivariate systems is through optimization, often involving statistical methods such as *design of experiments*. This is an effective tool when the needed information regarding the parameters affecting the system is

known. However, the diversity and intricacies of new and modified battery materials inherently reduce the probability of optimization experiments resulting in marketable products because operation mechanisms are unknown. Still undefined are the fundamental issues influencing ion and electron transport and electron transfer, how phenomena change across multiple domains including interfaces, and how transport phenomena evolve under flux in systems not at equilibrium. To achieve previously unrealized functionality at the working system level, understanding the critical roles of defects and interfaces in the underlying molecular and atomic structures and their interplay at the mesoscale is essential.^{2,3} In such cases, investigation over multiple length scales can provide the fundamental understanding that will lead to scientific insights.

This requires multiple characterization and theory approaches used in concert, to tie together information gathered at the local or atomic level through methods like transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), and X-ray powder diffraction (XPD); at the crystallite level with particle size (PS); with mesoscale information such as structure of the composite electrode via scanning electron microscopy (SEM) and transmission X-ray microscopy (TXM); with systems level performance from electrochemical impedance spectroscopy (EIS), galvanostatic intermittent titration type (GITT) test, galvanostatic cycling (GC), and related techniques, Figure 2. This outlook will argue that combining synthesis,

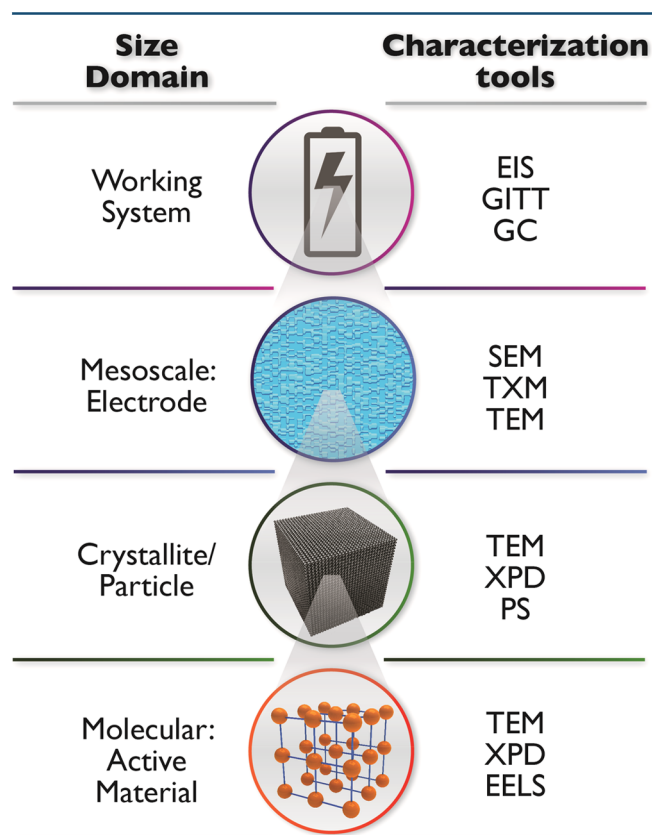


Figure 2. Size domain and characterization tools.

characterization, electrochemistry, theory, and modeling expertise to study batteries from the molecular to mesoscale level can lead to a complete understanding of battery function. A zero-dimensional active material, magnetite (Fe_3O_4), is used as an illustrative case study.

FUNDAMENTAL INSIGHTS VIA ATOMISTIC CHARACTERIZATION AND THEORY

Fe₃O₄ has been a material of particular interest for the expansion of the lithium ion battery into larger scale applications including electric vehicles and the grid in part due to its high abundance, low cost, and low toxicity.⁴ Fe₃O₄ along with other metal cation containing compounds, including metal oxides, fluoride, oxyfluorides, nitrides, and sulfides,^{5–9} has been shown to undergo multiple electron transfers (MET) for each metal cation. The MET reactions in these compounds enable higher energy density when compared to intercalation electrodes. When Fe₃O₄ has been fully reduced to Fe⁰ and Li₂O, it undergoes a complex process involving multiple phase transitions and is strongly dependent on the electrochemical environment.^{10–16} Previous X-ray diffraction (XRD) studies of phase transformation in Fe₃O₄ have suggested that there are multiple intermediate phases including the rock salt FeO¹⁷ or the rock salt like phase Li_xFeO₂.¹⁸ In addition to phase changes as a result of (de)lithiation, moderate volume changes occur (i.e., 15% from Fe₃O₄ to Li₂Fe₃O₄)¹⁶ which can lead to increases in resistance due to loss of electrical contact within an electrode or between the active material and current collector.

Due to the poor crystallinity of lithiated Fe₃O₄ materials, XRD analysis has been limited in its ability to determine the structure of the phases involved, so a complete description of the mechanism of Li and Fe ion migration during MET reactions has remained elusive. Advanced characterization techniques such as scanning transmission electron spectroscopy (STEM), electron energy loss spectroscopy (EELS) and electron diffraction can identify both chemical and structural changes with high spatial resolution (to the atomic level). In a recent study, annular-bright-field (ABF) STEM imaging was used, in combination with high angle annular-dark-field (HAADF) STEM imaging and EELS, to investigate the site occupancies of all species (including anions O²⁻ and cations Li⁺, Fe²⁺, and Fe³⁺), where a coherent orientation between FeO and Fe⁰ was observed in the highly reduced materials.¹⁶ One of the benefits of ABF imaging is its ability to directly visualize lighter elements such as Li⁺, as has been demonstrated in YH₂¹⁹ and LiFePO₄²⁰ systems.

When a battery operates, ions and electrons are transported over multiple size domains.

Notably, XRD techniques provide information on long-range ordering of the crystalline phases in the materials, but may not be suitable for characterization of structural changes in nanomaterials formed as a result of electrochemical reduction and oxidation, due to their small crystallite size and associated line broadening.^{21–23} In contrast, X-ray absorption spectroscopy (XAS) is an element specific technique allowing only atoms of interest to be probed, and so it can accurately characterize both crystalline and highly disordered materials. XAS methods have been previously used to determine detailed electrochemical mechanisms in electrodes that exhibit complex multistep processes, although amorphous phases were primarily involved.^{24–28} In general, XAS spectra contain two main regions, the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS), which are sensitive to the local electronic environment (i.e., oxidation state) and

neighboring atomic structure (coordination number, atomic identity, interatomic distance, etc.). The XANES region can be directly compared to the standards of known oxidation states to determine the average oxidation state of the element of interest within the sample, while the EXAFS region can be analyzed with theoretical structural models to extract details about the surrounding atomic environment within ca. 6 Å around the absorbing atom. A representation of the discharge mechanism gained from complementary experimental techniques including ex situ XRD, TEM, EXAFS, XAS, and HAADF/ABF is shown in Figure 3, where the progression of lithiation is indicated by *x*,

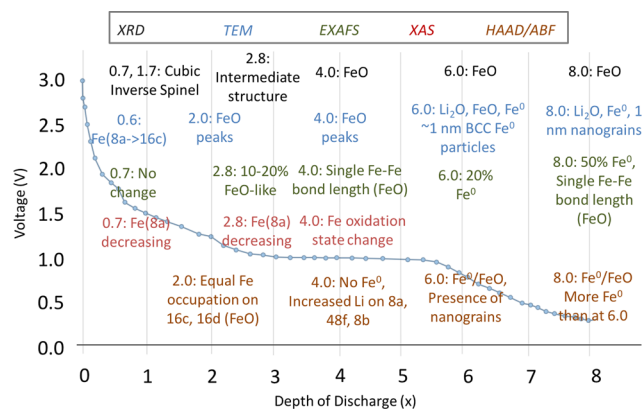
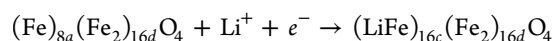


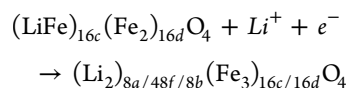
Figure 3. Discharge mechanism of Fe₃O₄ where *x* = electron equivalents.

which equals the molar equivalents of reduction. The overall reduction for Fe₃O₄ gleaned from using a variety of characterization techniques noted in Figure 3 is summarized in the scheme below showing the progression from reduction with lithium ion insertion to full conversion with formation of iron metal, Fe⁰, and lithium oxide, Li₂O.

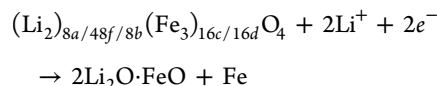
- (1) Reduction by one electron equivalent and insertion of one Li⁺ ion to form LiFe₃O₄:



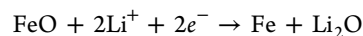
- (2) Reduction by second electron equivalent insertion of the second Li⁺ ion to form Li₂Fe₃O₄:



- (3) Additional reduction and insertion of lithium ions to form a composite Li₂O·FeO:



- (4) Full conversion reaction leading to metallic Fe⁰:



Density functional theory with the Hubbard correction (DFT+U) was applied for correlating the mechanism to structural ordering, where the partially lithiated Li₂Fe₃O₄ structure was shown to preserve the O anion framework with 15% volume expansion, consistent with the experimentally observed

structure by EXAFS.¹⁶ This study demonstrated that the cubic-close-packed (ccp) array of O anions was maintained during the process of lithiation and delithiation.¹⁶ Retention of the O anion ccp structure enabled multiple lithium intercalation and conversion reactions where partial reduction at less than 4 electron equivalents resulted in phase transformations from inverse spinel to rock salt like phases, with limited morphological changes. Upon further lithiation within the identified ccp O anion framework, local cation reordering occurred, leading to FeO phase and finally to a Fe/Li₂O nanocomposite phase.

■ IMPLICATIONS OF MESOSCALE CHARACTERIZATION AND MODEL DEVELOPMENT

Synthetic control of crystallite size has been demonstrated to increase the usable capacity by shortening the path length for Li ion diffusion, thus enhancing ion accessibility at higher discharge currents in previously reported metal oxide electrode materials.^{7,29–32} In particular, control of crystallite size has been shown to be important for densely structured materials, such as magnetite. A remaining challenge in realizing magnetite (Fe₃O₄) as a usable electrode in a lithium ion battery is to be able to achieve its high theoretical capacity.³³ Despite the improved capacity from efforts to synthetically control nanocrystalline magnetite including size³⁴ and morphology³⁵ to limit the path length required for Li ion transport, the theoretical capacity has not been uniformly reached.

Over time, resistance caused by phase changes in the solids and changes in the composition and structure of the interfaces can evolve, leading to inefficiency.

While prior studies have addressed crystallite size effects^{18,36–41} on the electrochemistry of crystalline Fe₃O₄, there have been

few reports that address agglomeration,^{42,43} which, due to the nature of active battery material being combined with a conductive additive and binder, is an avenue that warrants analysis and investigation. Additionally, while some of the above studies have indicated that agglomeration during cycling may correlate to electrochemical properties, they have not quantified agglomerate size or made direct correlations of its effect on the system performance.

Recently, a complete study of a nanocrystalline material in a battery electrode was conducted to provide a holistic view of the cell and considered both the crystallite size of the nanomaterial and the agglomerate size, Figure 4.¹ In order to evaluate a representative sample from an electrode, specimens were prepared using an ultramicrotome diamond knife to remove large parallel sections (1 × 2 mm) of the electrode, which were analyzed using TEM and quantified using image mapping techniques. Previously, sample preparation typically employed the use of a focused ion beam (FIB) to produce a thin lamella, which is then cut free from the bulk sample by use of a tungsten manipulator.^{44,45} The samples produced from FIB often ranged from 20 to 40 μm in size, and while local information relating to agglomerate size could be deduced, it was difficult to determine whether the particular sample was representative of the bulk material.

The combination of sample preparation using an ultramicrotome and characterization using TEM combined with 2D mapping by transmission X-ray microscopy (TXM) and X-ray absorption near edge spectroscopy (XANES) provided a comprehensive two-dimensional map, showing the distribution of iron, and its corresponding oxidation states both before and after cycling. Mapping techniques such as TXM–XANES provide information on the distribution of oxidation states of the samples over a large sample area. While it was found that the smaller crystallite size Fe₃O₄ displayed more uniform discharge, agglomerate size of the sample was not found to depend on crystallite size, as previously suspected from prior work on particle size of powders.^{38,39}

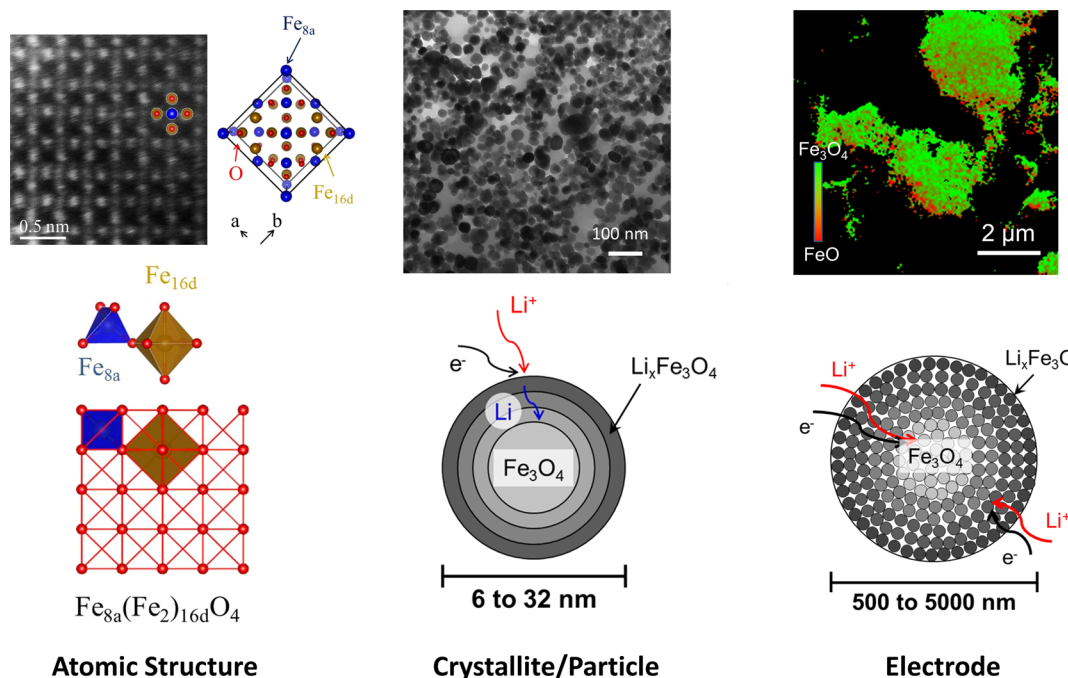


Figure 4. Multiscale characterization and theory for Fe₃O₄.

The identification of agglomerates has led to the electrode being categorized into varying length scales with different corresponding properties. In concert with the overarching theme of microscale to mesoscale in understanding battery performance, the three length scales existing within the electrode have been identified as the bulk electrode (macroscale), the agglomerates (mesoscale), and crystals (nanoscale).^{33,46} Recent work describes a model that investigates the various performance-limiting processes of magnetite at these varied length scales.³³ One of the aims of this work was to correlate and support proposed, multifaceted models to experimental data to understand crystal versus agglomerate. Initially, the voltage recovery of Fe_3O_4 was evaluated mathematically and experimentally for 6 nm crystals synthesized by the previously reported coprecipitation method.^{38,39} Time constant analysis was used to compare the concentration relaxation times associated with the agglomerate and crystal length scales, and describes the time that is required for the system to relax after a step change in concentration at one boundary location.⁴⁶ Time constants were compared to determine the primary length scale (agglomerate or crystal), and diffusion coefficients were determined using radii obtained from TEM images as representative lengths. Through verification with experimental data, results demonstrated that mass-transport constants can be useful to elucidate which local scale within the magnetite electrode contributes to the voltage recovery process.

To achieve previously unrealized functionality at the working system level, understanding the critical roles of defects and interfaces in the underlying molecular and atomic structures and their interplay at the mesoscale is essential.

The above model was expanded to perform a more in-depth study to evaluate how ion transport will affect the electrochemical performance in both the agglomerate and crystal length scales.³³ In addition to the previous reports on the voltage recovery of 6 nm magnetite, the newly proposed model was compared with experimental data from 8 and 32 nm magnetite samples. With the 6 and 8 nm Fe_3O_4 samples,

voltage recovery was found to stem from relaxation on the agglomerate scale, while in 32 nm crystals the voltage recovery was affected by both (agglomerate and crystal) length scales. While past literature has used modeling as a tool for a range of lithium ion batteries and electrodes,^{47–60} as far as the authors know, reported values for Li ion diffusion coefficients in crystals or aggregates of Fe_3O_4 do not exist in the literature.

Recently, a complete study of a nanocrystalline material in a battery electrode was conducted to provide a holistic view of the cell and considered both the crystallite size of the nanomaterial and the agglomerate size, Figure 4.

In light of the insights provided by the multiscale performance model of Fe_3O_4 containing electrodes,³³ a recent study⁶¹ was performed with the aim of reducing agglomeration of Fe_3O_4 as a means of improving lithium ion transport rates and, thus, delivered capacity. Agglomeration was effectively suppressed in Fe_3O_4 /carbon black composite electrodes by using oleic acid as a dispersing agent. A heat treatment process was then used to remove the oleic acid, which was found to result in unfavorable performance, while maintaining Fe_3O_4 dispersion in the carbon black matrix. Thus, in agreement with the performance model simulations, the composite electrodes with dispersed Fe_3O_4 initially delivered a higher functional capacity compared to the electrodes with aggregated magnetite under similar rates of discharge, Figure 5. However, upon extended cycling, the dispersed material exhibited increased capacity fade relative to the agglomerated Fe_3O_4 composites, Figure 5. X-ray absorption spectroscopy measurements of electrodes recovered from cells cycling along with complementary electrochemical impedance spectroscopy data facilitated a mechanistic explanation of the observed performance. After cycling, the dispersed Fe_3O_4 was more oxidized in the discharged state and had higher charge transfer resistance, suggesting that increased surface film formation on the highly dispersed material causes reduced reversibility.

The examples provided here affirm that multiscale characterization of Fe_3O_4 composites is critical for full understanding of electrochemical performance. Detailed insights into the

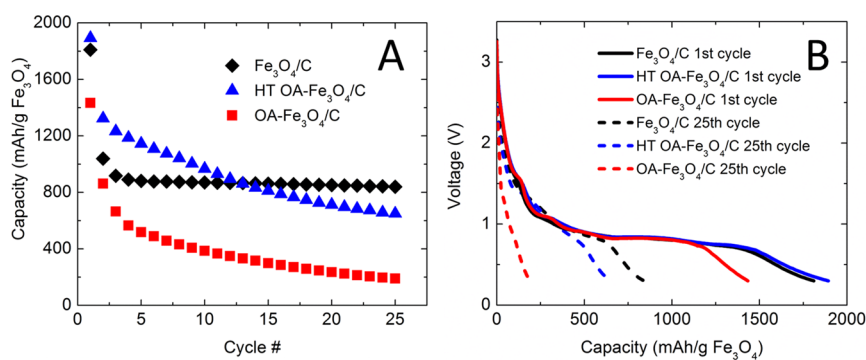


Figure 5. (A) Specific capacity versus cycle number at C/8 rate and (B) representative discharge profiles at cycle 1 and cycle 25 for Fe_3O_4 physically mixed with carbon ($\text{Fe}_3\text{O}_4/\text{C}$), oleic acid capped Fe_3O_4 dispersed in carbon black (OA- $\text{Fe}_3\text{O}_4/\text{C}$), and heat treated oleic acid capped Fe_3O_4 in dispersed in carbon black (HT OA- $\text{Fe}_3\text{O}_4/\text{C}$).

Advances in functional energy content and reduced cost will be achieved through the use of multiscale characterization methods linked with theory and modeling in the course of identifying and introducing new materials.

performance of Fe_3O_4 as an anode material will help enable realization of its promise as an anode material with a theoretical capacity $\sim 2.5\times$ higher than that of standard carbon anodes currently used in lithium ion batteries. A review of recently reported capacities of Fe_3O_4 based batteries shows that their functional capacities range almost 10-fold when configured into a variety of heterostructures, Figure 6.¹⁰ Notably, the theoretical

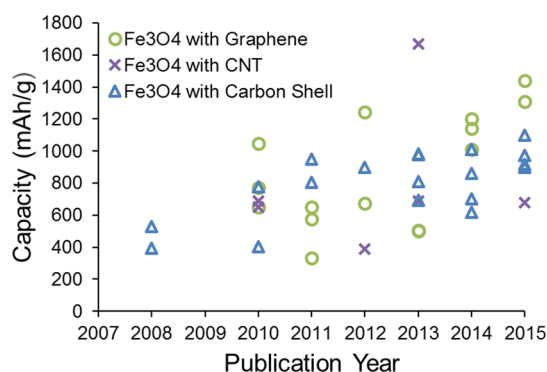


Figure 6. Capacity as a function of publication year for Fe_3O_4 based batteries.

first discharge capacity of Fe_3O_4 is 924 mAh/g, thus additional capacity is contributed by the carbon component of the heterostructure.

FINAL COMMENTS

Energy storage is an important field as it impacts society in diverse ways ranging from the convenience of portable electronic devices to the positive environmental impacts gained from integration of renewably generated energy and the adoption of electrified vehicles. Advances in functional energy content and reduced cost will be achieved through the use of multiscale characterization methods linked with theory and modeling in the course of identifying and introducing new materials. Understanding the complexity of the structural evolution, phase changes, and interfacial and surface phenomena of the active materials upon storage and electrochemical reduction and oxidation would provide additional insight into exploiting desired properties of the system to create better performing batteries. Systems with the complexity of electrochemical energy storage devices benefit from research efforts fostering multidisciplinary cooperation in the pursuit of their understanding. Use of multiscale characterization tools coordinated with theory/modeling approaches can assist in the elucidation of the mechanisms responsible for the observed performance and ultimately provide rational means of identifying, studying, and combining the appropriate battery components to fully enable the energy storage device toward a specific application.

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Notes

The authors declare no competing financial interest.

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