Assessing the Binding of Sodium Ions to a Maghemite Nanoparticle Surface for Applications in Sodium-Ion Batteries

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Lithium-ion batteries are currently the leading technology in energy storage. However due to limited availability of lithium, other more sustainable storage technologies are needed. One such promising storage technology is sodium-ion batteries. Sodium has similar properties as lithium given both are alkali metals while also being more readily available. We researched the binding of sodium ions to the surface of maghemite (γ-Fe2O3) nanoparticles as a first look for their viability as cathode material in sodium-ion batteries. Modeling both a maghemite nanoparticle sphere and the interactions that took place when a sodium ion was placed on its surface, we found that there was enough steric space on the nanoparticle surface to fit sodium ions. We also found binding energies of near -9.56 eV. Our results show that while the sodium ions could fit and bind on the nanoparticle surface, they did not stay for prolonged periods of time and future research is needed to build a deeper understanding of the complex interactions between sodium ions and maghemite nanoparticles.

Keywords: Sodium Ion, Molecular Dynamics, Maghemite Nanoparticle, Binding Energy, Surface Interactions

Introduction

Lithium-ion batteries are currently used widely ranging from grid-connected storage to electric vehicles to mobile devices [1]. But the sodium-ion battery has the potential to become a replacement as sodium is found in abundance in the earth's crust unlike lithium whose supply continues to diminish [2]. Moreover, sodium shares many chemical properties with lithium as they are both alkali metals which could allow sodium-ion batteries to meet and even surpass the efficiency of lithium-ion batteries [2–4].

What makes lithium-ion batteries so efficient is their distribution of power density (energy output) and energy density (energy storage) [5,6]. One way to achieve an efficient balance is through choice of battery material for the three main parts of the battery, namely the cathode, the anode, and the electrolyte. Previously, research has been conducted on the use of transition metal-oxides in both the cathode and the anode [7–10]. There are also a wide variety of materials being used in the electrolyte such as sodium salts, linear and cyclic carbonates, and film formers [11].

Another class of materials being considered are nanoparticles because of their potential to fix major drawbacks in sodium-ion battery design such as low conductivity [12]. The benefits of nanoparticles stem from their greatly increased surface area. This increased surface area allows for more interactions between the electrolyte and the electrodes leading to a higher ion transfer rate [13].

Maghemite nanoparticles show promise due to their low cost, ease of fabrication, and low toxicity [14]. Additionally, they have a high specific capacity of up to 1007 mAh/g [14]. On the other hand, other cathode materials such as layered oxides and Prussian blue analogs have lower specific capacities of up to 400 mAh/g and 170 mAh/g respectively [15,16]. Maghemite nanoparticles have been researched previously for use in lithium-ion batteries, but not yet for sodium-ion batteries.

We researched how maghemite (γ-Fe2O3) nanoparticles interact with sodium ions as a first look at their viability as cathode material in sodium-ion batteries. To accomplish this, we measured the surface dimensions of a nanoparticle sphere. Comparing it to the radius of a sodium ion, we found that there was enough steric space to fit a sodium ion in the nanoparticle's surface cavities. Then we modeled the interactions between the sodium-ion and maghemite nanoparticle surface, finding high binding energies which showed that maghemite nanoparticles could feasibly bind to sodium ions.

Methods

We started by measuring the dimensions of the surface cavities on a maghemite nanoparticle to determine whether sodium ions could fit. To do this, we built a nanoparticle sphere based on SEM and TEM data from past research and measured the distances between atoms close to the surface [17]. Then, we put sodium ions at different surface positions on this structure and found their initial binding energies. We then ran Molecular Dynamics with sodium ions starting at locations with the highest

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binding energies.

To run the Molecular Dynamics, we used the Atomic Simulation Environment (ASE 3.23.0) and Velocity Verlet[18]. The latter was chosen because of stability during long simulations. Velocity Verlet is an extension of the Verlet algorithm which integrates Newton's equation of motions to calculate the trajectories of particles. Unlike the basic Verlet algorithm which only keeps track of the positions of the particles, Velocity Verlet stores the velocity as well as the acceleration. In our Molecular Dynamics simulation, we set the time step to 50 fs and ran the simulation for a total of 50 steps.

To set up the environment for the simulation, we used the Maxwell-Boltzmann distribution which describes initial velocities of particles based on a given temperature. Generally, as temperature rises the initial velocities increase as these values are directly proportional. In our case, we ran the simulation at temperatures of 250 K, 300 K, and 350 K. Additionally, because lighter particles move faster than heavier particles, lighter particles will have faster speed distributions as well as a more spread out distribution.

During the simulation, the Lennard-Jones potential was used to calculate the forces created by the interactions between the sodium particles and the maghemite nanoparticle surface. The Lennard-Jones potential calculates the forces using the distances between the particles. At the core, close-by particles repel, medium distance particles attract, and particles further and further away stop interacting. The potential also takes into account two key parameters: epsilon (ε) and sigma (σ). ε (relative minimum) is the depth of the potential energy well and σ is the distance at which the potential energy between two particles is zero. We set ε to 0.0276 eV (2.657484 kJ/mol) and σ to 2.47 $\mathring{A}$ based on previous literature[19].

For more details regarding the example algorithms and visualization techniques employed, see the code in the data availability section.

Results

Nanoparticle Structure

We began our analysis by studying whether the ion could bind within surface facets of the nanoparticle based upon geometric/steric conditions, i.e., without considering electrostatic interactions. To do so, we sourced an iron oxide structure from the Crystallography Open Database (CIF = 1528611) that corresponds to maghemite[17]. The spherical nanoparticle model we carved out in VESTA contained a total of 2,011 atoms, comprising 807 iron (shown in brown) and 1,204 oxygen (shown in red) atoms, resulting in an average nanoparticle radius of 16.19 $\mathring{A}$ in VESTA (see Figure 1). A sodium ion was added near the nanoparticle surface at the position (9.5, 5.3, 11.5), which is 1.73 $\mathring{A}$ away from the surface. The distances between the sodium and nearby oxygen atoms were measured using VESTA's built-in distance tool, yielding values of 1.86 $\mathring{A}$, 1.86 $\mathring{A}$, 1.73 $\mathring{A}$, and 1.83 $\mathring{A}$. The average distance was then calculated to be 1.82 $\mathring{A}$. The radius of a sodium ion is 0.53 $\mathring{A}$ which is within the average distance between the ion and nanoparticle quantified above[20]. Based on these calculations, there is enough space for the sodium ion to fit at the surface, which is a first check on the viability of sodium ions binding to the nanoparticle surface.

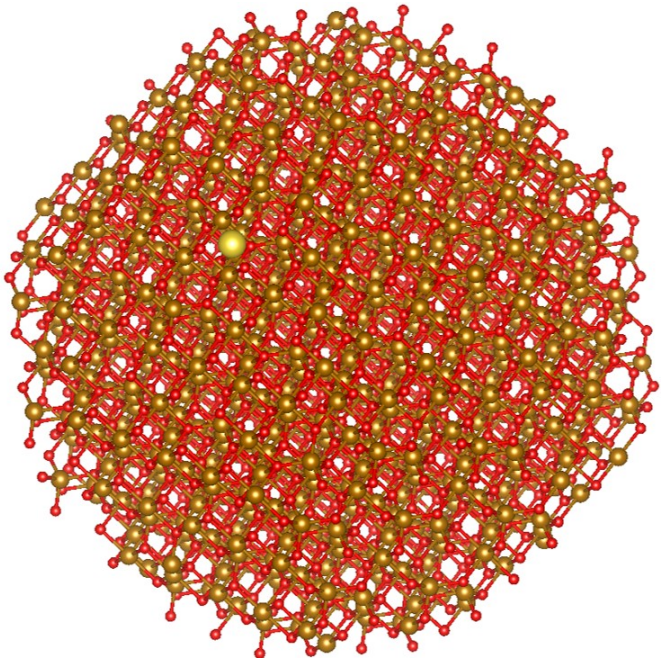

Fig. 1 Maghemite nanoparticle with a sodium ion (yellow) added to the surface visualized in VESTA.

Binding of Sodium Ion to the Nanoparticle Surface

We next incorporated electrostatic interactions into our binding analysis to make it more realistic by studying the interaction energy between the ion and the surface at various positions across the nanoparticle. We used VESTA to visualize the binding of sodium at different positions around the surface. Then, we placed the sodium ion at different z coordinates, moved them along the xy-plane, and analyzed the minimum energies obtained. The nanoparticle center was at (0$\mathring{A}$, 0$\mathring{A}$, 0$\mathring{A}$) and the energy of the nanoparticle was 4578.47 eV. Some of the more stable surface positions include (5.99$\mathring{A}$, 13.99$\mathring{A}$, 9.5$\mathring{A}$) with a potential energy of -56.74 (Figure 2a) and (-10.51$\mathring{A}$, 12.99$\mathring{A}$, 2$\mathring{A}$) with a potential energy of -9.62 eV (Figure 2b). Because Molecular Dynamics simulations are stochastic, they were repeated multiple times to ensure statistical confidence. Similar results can be found in the Appendix.

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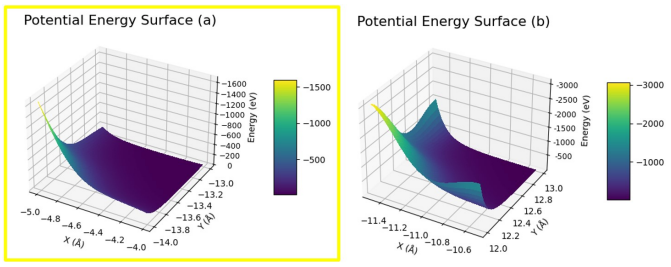

Fig. 2 The potential energy surface of the sodium ion moved across the surface of the nanoparticle in the xy-plane. (a) The minimum energy found was -9.57 eV at the location (-4.21*Å*, -13.2*Å*, -7*Å*). (b) The minimum energy found was -9.62 eV at the location (-10.51*Å*, 12.99*Å*, 2*Å*).

Molecular Dynamics of Nanoparticle-Ion Structures

We analyzed the motion of the sodium atoms after being bound to the surface at different initial starting positions using Molecular Dynamics simulations. Unlike the potential energy surfaces presented above, these simulations accounted for entropy and temperature by also providing the particles with an initial kinetic energy. Molecular Dynamics is a better arbiter of how stable binding will be at realistic temperatures, and thus this work built upon the previous section in terms of realism.

In Figures 3, 4, and 5, we show snapshots from a few illustrative trajectories that were initiated at the minimum energy positions identified above at 300 K, 250 K, and 350 K respectively. In Figure 3, the sodium was initially stable for the first 450 fs, but by 500 fs it left the nanoparticle surface because its interactions as a neutral species (it was not charged in these simulations) with the nanoparticle weren't strong enough to keep it bound. Similarly, in Figure 4, the sodium was stable for the first 400 fs and left by 450 fs. However, in Figure 5, the sodium was only stable for the first 200 fs and left by 250 fs. This suggests that as temperature increases, the stability decreases significantly while when the temperature decreases the stability only decreases slightly.

Discussion

The findings from our simulations offer insights into the interactions between sodium ions and maghemite nanoparticles. However, several limitations in the simulation setup must be acknowledged before drawing broader conclusions about sodium ions and maghemite nanoparticles in real-world sodium-ion battery applications.

The major limitation lies in the version of the Lennard-Jones potential we employed. While effective for capturing certain electrostatic interactions, it overlooks the charge of the sodium ion. In reality, sodium ions are positively charged, which would lead to stronger interactions with the maghemite nanoparticle

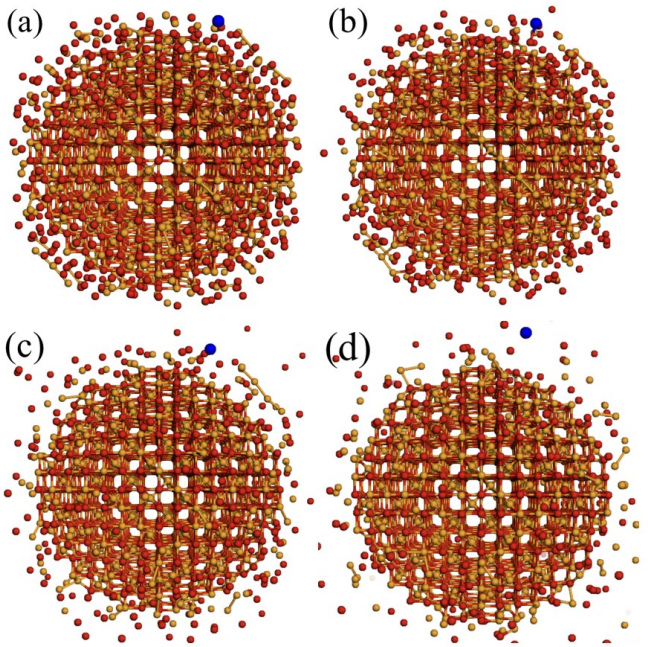

Fig. 3 Simulation of a maghemite nanoparticle at 300 K with sodium ion (blue) inserted at the location (5.99*Å*, 13.99*Å*, 9.5*Å*). The location of the sodium ion in regards to the nanoparticle: (a) at 50 fs; (b) at 150 fs; (c) at 250 fs; and (d) at 500 fs.

surface, which could also carry a charge. Ignoring these charge-based interactions in the simulation likely impacted the calculated binding energies and the movement of the sodium ions. Without considering the sodium ion's charge, the model simplified the real forces acting in the system. Incorporating more accurate electrostatic potentials or using more advanced methods such as Density Functional Theory (DFT) in future studies would provide a more realistic and accurate representation of the interactions between sodium ions and the nanoparticle surface.

The second limitation of our simulation was that it did not fully factor in all elements of a realistic environment. We modeled the maghemite nanoparticles and sodium ions and their interactions without taking into account other key parts of a battery. For example, we did not model an electrolyte, leaving out interactions between the nanoparticle and electrolyte and the sodium ion and electrolyte which would influence the interactions between the nanoparticle and the sodium ion.

Conclusions

We researched the use of maghemite nanoparticles in sodium-ion batteries to test if they were suitable cathode material. We measured the dimensions of cavities on the nanoparticle surface, placing the sodium ion at various positions. We found that the average distance between the sodium ion and nearby oxygen

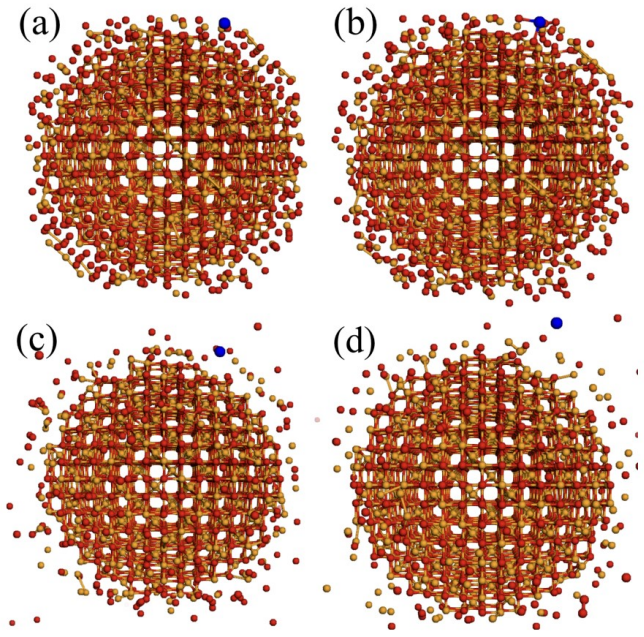

Fig. 4 Simulation of a maghemite nanoparticle at 250 K with sodium ion (blue) inserted at the location (5.99*Å*, 13.99*Å*, 9.5*Å*). The location of the sodium ion in regards to the nanoparticle: (a) at 50 fs; (b) at 150 fs; (c) at 250 fs; and (d) at 450 fs.

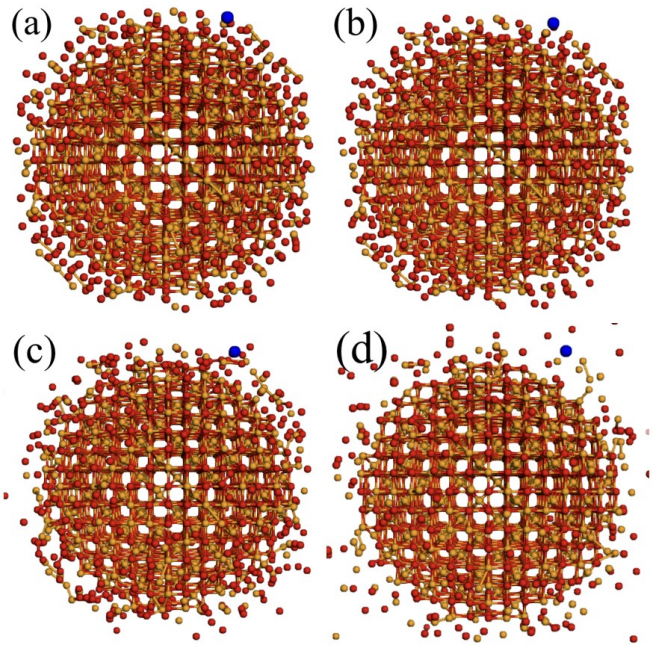

Fig. 5 Simulation of a maghemite nanoparticle at 350 K with sodium ion (blue) inserted at the location (5.99*Å*, 13.99*Å*, 9.5*Å*). The location of the sodium ion in regards to the nanoparticle: (a) at 50 fs; (b) at 100 fs; (c) at 150 fs; and (d) at 250 fs.

atoms was 1.82 *Å*. As the average radius of a sodium ion is 0.53 *Å*, we concluded that there was enough steric space on the surface.

To gain a more accurate understanding of sodium ion behavior, we ran Molecular Dynamics initializing particles at the identified energetic minima associated with various placements of the sodium ions. Some binding energies obtained include -9.56 eV when the sodium ion was placed at (-6.31*Å*, 13.7*Å*, -3*Å*) in regards to the center and -9.62 eV when the sodium ion was placed at (-10.51*Å*, 12.99*Å*, 2*Å*). However, the Lennard-Jones potential that was used in our simulations did not account for ion charge. This led to the results showing that the sodium ions were not stable as they left the surface after 450 fs at 300K, 400 fs at 250 K, and 200 fs at 350 K. This suggests that, while structural compatibility exists, other factors—such as charge interactions and environmental conditions—play a crucial role in stabilizing these ions. In future work we would also like to validate the SEM and TEM data against electrochemical and additional microscopy experiments as well as more rigorously test the effects of temperature on stability.

The implications of this study are significant, especially as sodium-ion batteries emerge as an alternative to lithium-ion batteries. With sodium's natural abundance and favorable chemical properties, advances in this field could lead to more sustainable energy storage solutions. This research serves as a first look into the use of maghemite nanoparticle cathodes in enhancing sodium-ion battery performance.

Data and Code Availability Statement

The code used to generate this data may be found at: https://colab.research.google.com/drive/1SYhvttECQhDW1FZVxE-dze9XYF3Os8LI?authuser=1#scrollTo=GQ0H-siXI4I9

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Appendix 1 Replicates

Replicates of minimum energy calculations and positions on the nanoparticle surface:

Table 1 Sodium Ion Position and Minimum Energy

Sodium Ion Position (xÅ, yÅ, zÅ)	Minimum Energy (eV)
(-10.51, 12.99, 2)	-9.62
(-4.21, -13.2, -7)	-9.57
(10.51, 12.5, 2)	-9.62
(-4.21, 13.8, -9.5)	-9.57
(-6.31, 13.7, -3)	-9.56
Average minimum energy: -9.588 eV	

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