Magnetic and Structural Investigation of Electrochemically Lithiated Magnetite Nanoparticles

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Magnetite Fe_3O_4, a spinel structure (Fd3m), has interesting properties such as room-temperature ferrimagnetism, high Curie temperature, and spin polarization. The reasonable electrical conductivity of magnetite opens the possibility of modifying the saturation magnetization by inserting Li^+ ions into the structure, in a process similar to that used in conventional lithium batteries. In this study, we have measured the effects of electrochemical lithiation on the structure and magnetic properties of magnetite nanoparticles. A decrease in M_s of up to 75% was observed upon addition of 2 moles of Li per formula unit, along with changes in remanence and coercivity. The insertion of Li^+ changes the moment by altering both the valence states and the locations of the Fe ions within the structure, and a model is proposed to explain the observations.

Index Terms—**Ferrimagnetic, magnetite, nanoparticles, spinel.**

I. INTRODUCTION

TRANSITION metal oxides (TMOs) comprise a fascinating class of materials that display a wide range of magnetic and electronic properties. These range from half-metallic ferromagnets like CrO_2 to antiferromagnetic insulators such as rocksalt-structured FeO. An important TMO is magnetite Fe_3O_4. It is the oldest magnetic material known to man, but it has many properties that pique curiosity even today. It is a room-temperature ferrimagnet with a high Curie temperature and a high degree of spin polarization, which makes it attractive for spintronics.

Magnetism in TMOs such as Fe_3O_4 is due to coupling of spins of cationic 3d electrons via superexchange mediated by the intervening anion. The accessibility of multiple electronic configurations and coordination of cations in these compounds enables the tuning of magnetism by an external stimulus.

One such stimulus is the insertion of Li^+ ions into the structure, which can reduce the valence states of cations, alter the metal–oxygen–metal (M–O–M) bond angles and M–O bond distances, and possibly also the coordination of transition metal ions in the structure. This can be investigated experimentally by electrochemical discharge of a Li battery consisting of the transition metal oxide as cathode. In this study, we have studied the effect of electrochemical lithium insertion on the magnetic properties of Fe_3O_4 nanoparticles.

Earlier studies on lithiation of magnetite powders to form $Li_xFe_3O_4$ have shown that it is possible to insert up to $x = 2$ of Li before commencement of a displacement reaction involving formation of metallic iron [1]. There is also evidence for a spinel-to-rocksalt transformation as lithiation proceeds [2]–[5] resulting from cooperative displacement of tetrahedral Fe ions into 16c sites induced by electrostatic repulsion [6]. This should result in complete disappearance of the magnetic moment at room temperature, since the rocksalt phase is expected to have a Curie temperature of 150 K [2]. The aim of the present study is to study the effect on magnetic properties of inserting different amounts of Li into commercially available Fe_3O_4 nanoparticles by discharging them down to different voltages and to propose a model for the same.

II. EXPERIMENTAL METHODS

A. Electrochemical Lithium Insertion

Composite thick-film cathodes roughly 30 μm in thickness were prepared by casting a mixture of magnetite nanopowders (Alfa Aesar, mean size 65 nm), SUPER P^{TM} conductive carbon black and poly-(vinylidene fluoride) (PVDF) in the weight ratio 11:6:3 on aluminium substrates, and punching out circular disks [7]. The starting magnetite powders contain hematite, corundum-structured α-Fe_2O_3 as an impurity, which is estimated to be around 15% from the ratio of intensities of XRD peaks and measurement of saturation magnetization M_s [7]. The cathodes were dried, weighed, assembled into cells in an argon-filled glovebox, and subjected to galvanostatic electrochemical discharge to voltages in the range 1.0 to 1.7 V. This resulted in samples with lithium contents between $x = 0.01$ and $x = 2$. Details on the procedure can be found in [7].

B. Structural and Magnetic Characterization

Room temperature magnetic measurements were done on the cathodes pre- and post-lithiation using an ADE 880 vibrating sample magnetometer by applying fields in the range between -10 and 10 kOe. Structural changes were tracked by $\theta - 2\theta$ X-ray diffraction using a Rigaku RU300 X-ray generator and 185-mm diffractometer. The scans were done in helium flow immediately post-lithiation. The intensity of (111), (220), (311), and (440) spinel peaks and the main (104) hematite peak were tracked for the samples lithiated to different extents. The effect of lithium insertion on the Curie temperature was measured by cycling the cathodes between 313 and 913 K in a furnace immediately post-lithiation. An external magnetic field of 6 kOe was applied to saturate the sample, and a helium flow was maintained in the measurement.
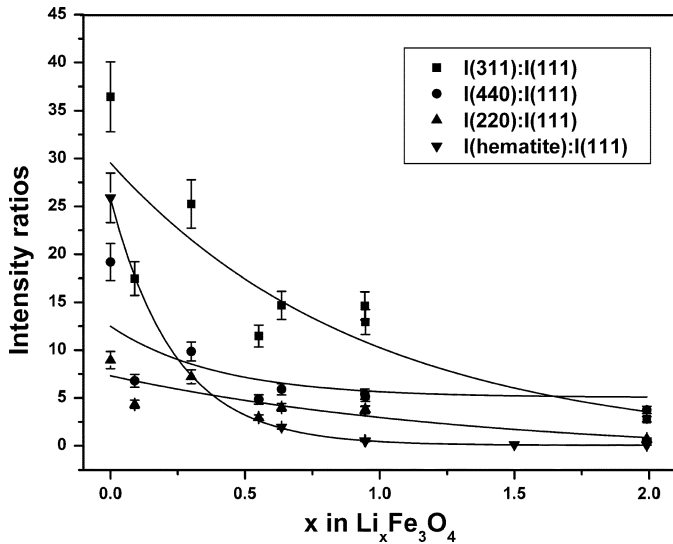
Fig. 1. Intensity ratios of various spinel and hematite peaks as a function of lithium content. The lines serve as a guide to the eye.

III. RESULTS AND DISCUSSION

A. Structural Investigation

The XRD data are shown in Fig. 1. It is expected that the spinel peaks change in relative intensities as lithiation proceeds, due to formation of the rock salt structure from the spinel framework [2]. The ratios of (220), (311), and (440) peaks of the spinel and the hematite (104) peak to the (111) spinel peak intensity are shown in Fig. 1 as a function of lithium content. It is clear that the hematite phase is transformed, since this peak decreases in intensity and vanishes completely by $x = 2$. The hematite/(111) peak ratio decreases from 26.0 at $x = 0$ to 0.5 at $x = 1$. Also the magnetite (311)/(111) ratio decreases from 36.6 at $x = 0$ to 2.85 at $x = 2$. The (220)/(111) peak ratio decreases from 9.0 at $x = 0$ to 0.6 at $x = 2$. The decrease in the (440)/(111) and (220)/(111) intensity ratios is in agreement with the mechanism proposed in the literature which involves cooperative displacement of Fe ions from the tetrahedral sites into octahedral sites [6].

B. Room-Temperature Magnetic Properties

Fig. 2 shows the hysteresis loops of a sample discharged to a composition of $Li_{1.75}Fe_3O_4$. The coercivity and loop shape are largely unchanged but the M_s has decreased by 53.4%.

The results of room-temperature magnetic measurements on lithiated nanoparticles are summarized in Fig. 3. It is clear that the saturation magnetization decreases as lithiation proceeds, dropping to 29.2% of the original value at $x = 1.99$. We note that there is not much change in the saturation moment in the regime $x = 0$ to $x = 1$. This is an unexpected result, since the magnetization is predicted to decrease monotonically in lithiated magnetite [3]. There is negligible change in the remanence M_r/M_s, except for a small rise in the beginning and beyond $x = 1.5$. The coercivity shows no change until $x = 1.5$, beyond which it starts to decrease.

The magnetic moment of magnetite is expected to decrease upon lithiation because of the formation of the paramagnetic
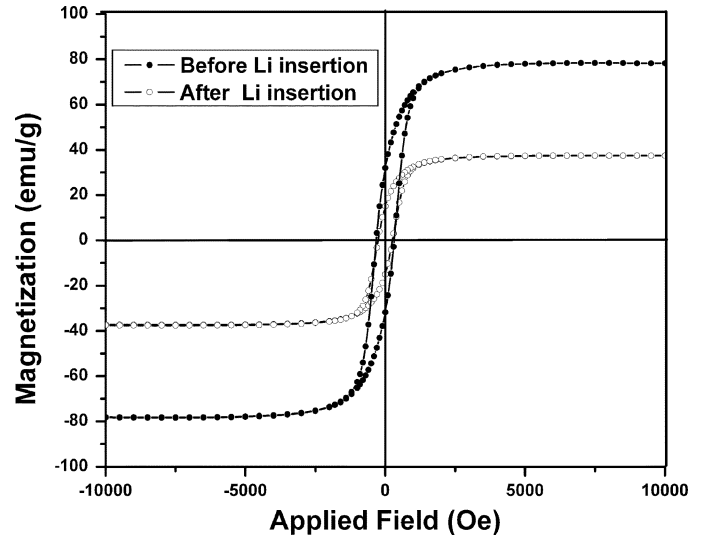

Fig. 2. M–H curve of a cathode discharged down to $x_{Li} = 1.748$ at a current density of 3.37 $\mu A/cm^2$ before and after lithiation.
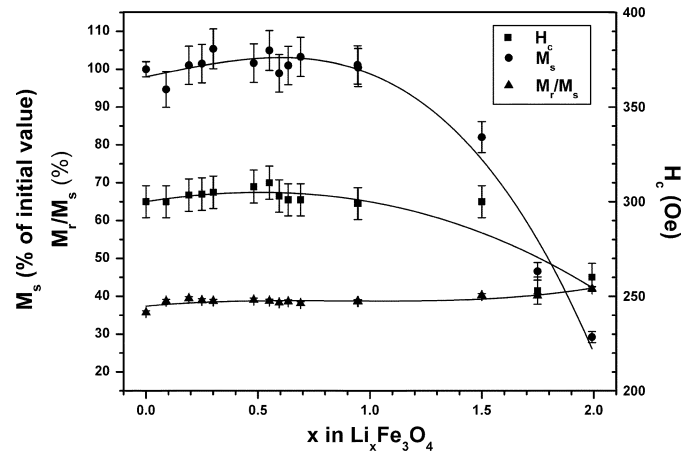

Fig. 3. Variation of saturation magnetization, coercive field, and remanence with lithium content. The error bars denote the experimental errors.

rocksalt phase beyond a critical concentration of Li. The hematite will get converted from the hcp (corundum) structure to a ccp (rock salt) structure [1]. Larcher et al. have shown that the onset of the hcp-to-ccp transition that occurs in micrometer-sized hematite immediately upon lithiation is delayed until $x = 1$ for pure hematite nanoparticles of mean size 20 nm [8], [9]. This may explain the negligible changes in magnetization that we have observed in the regime $x = 0$ to 1. In the initial stages, there might be competition between the Li insertion reaction into magnetite and the monophasic insertion reaction into hematite [8], [9]. This is consistent with the XRD data, in which the hematite peaks are observed to decrease in intensity and disappear almost completely by $x = 1$. This coincides with the onset of decrease in M_s, when presumably there is no competition for the Li insertion reaction into magnetite. In addition, researchers have shown that the spinel-to-rock-salt phase transformation is suppressed in nanosized γ-Fe_2O_3 [10]. It is possible that nanosized magnetite undergoes a similar topochemical reaction mechanism. If so, this could also explain the anomaly in the variation of M_s.
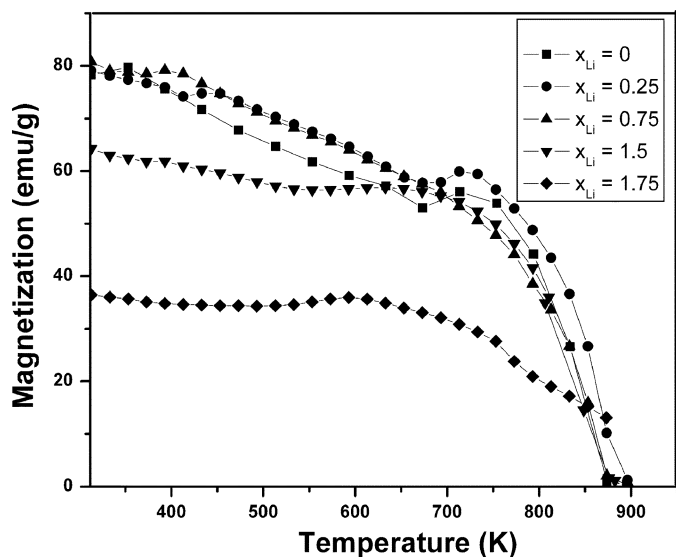
Fig. 4. Summary of Curie temperature measurements on samples discharged to different extents. Here x_{Li} denotes the number of moles of lithium inserted.

C. Curie Temperature

The results of Curie temperature measurements are summarized in Fig. 4. The curve for the cathode prior to lithium insertion has an upward slope around 720 K. This anomalous behavior is seen in some samples, while it is absent in others. These features disappear upon cooling back down, so in all probability, this is a result of an irreversible phase transformation upon heating. The source of this anomaly is unclear. However, Xu *et al.* point out that the annealing of superparamagnetic particles can contribute to an anomalous increase in magnetization with increase in temperature [10]. It is possible that the presence of a small fraction of superparamagnetic particles in our starting powders could cause such behavior. However, the Curie temperatures unexpectedly remain close to that of bulk magnetite, which is 860 K, even though the moment decreases. This suggests that a fraction of the material not transformed completely into the rock salt phase, due to kinetic limitations. The cores of the nanoparticles probably remain unlithiated.

IV. CONCLUSION

Ferrimagnetic Fe_3O_4 nanoparticles were inserted with different concentrations of Li by galvanostatic discharge. The magnetization is expected to decrease due to formation of paramagnetic rock salt phase. However, this should result in zero net magnetization upon completion of the phase transformation. Although a substantial decrease in M_s was observed upon inser-

tion of more than one mole of Li per formula unit, room-temperature magnetic measurements and Curie temperature measurements suggest that there are negligible changes in magnetization until $x = 1$. This maybe explained by the presence of hematite as the impurity phase, which could be reacting with some of the lithium in the early stages. Also, there might be suppression of the spinel-rock salt phase transformation due to small size of the particles.

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