Research Article

Influence of Lithium on Nanosized Films of Fe₂O₃

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We have investigated nanosized thin films of α -Fe₂O₃ (hematite) and α -Fe₂O₃ with addition of Li, by the impedance spectroscopy (IS), the Raman spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Combining all of these methods, and earlier obtained thermally stimulated currents (TSC) on the same samples, the dependence of structural and electrical properties upon percentage of Li added into the matrix of these metal-oxide films was found. The comparison of IS, Raman, SEM, XRD, and TSC results reveals the increase of the size of nanoparticles upon inducing 1% of Li in Fe₂O₃ matrix followed by the decrease of the size of nanoparticles in the case of samples with 10% Li, as well as the decrease (increase) of conductivity, respectively. These changes are explained by the structural and morphological changes caused by the impact of Li⁺ ions in the charge transfers. This material is suitable for application in the galvanic cell of second generation that could be used as solar-cells backup.

1. Introduction

Thin-films containing nanosized grains of Fe₂O₃ are widely used in research into mainly magnetic and electronic devices [1–5]. Their capacity for incorporating lithium ions is important in the construction of galvanic cells of second generation [6–17].

The one of newest and attractive application of Fe based batteries as high capacity LiFePO₄ and LiFeYPO₄ cells would be in electric vehicles [18]. Our intention is to construct charge-discharge Fe₂O₃-electrode battery with polymer electrolyte [19, 20]. Further plan is to attach it to solar-cells [21–24] in order to preserve accumulated charge to use it in cloudy weather.

Films of iron oxide derived by the chemical deposition method route were investigated by the impedance spectroscopy (IS), Raman spectroscopy, SEM, and XRD in order to determine their electrical, structural, and morphological properties. Our goal was to establish the relation between electrical and the structural properties in nanostructured Fe₂O₃ and Fe₂O₃:Li films on glass substrate.

IS was applied to measure the resistance of nanostructured Fe₂O₃ films with different contents of lithium. In our previous work [25], TSC spectra, often used in characterization of high resistive or semi-insulating (SI)

materials [26, 27], were measured on the same samples, in order to investigate possible defects with deep levels in the forbidden energy gap and to see relation of it to the different percentages of Li.

By Raman and XRD measurements, we have determined, besides the hematite nature of our samples, that they are composed of the nanosized crystalline grains in the size range from 10 nm to 200 nm, which was also proved by SEM investigation. It was also found that the variation of Li⁺-ion content is related to the changes of the nanoparticles ($d < 5$ nm) related to the acoustic phonons determined by the low frequency Raman measurements. We have also found samples' steadiness during the eight-month period.

2. Experimental

The samples were nanostructured Fe₂O₃ films deposited on the glass substrates and were prepared using chemical vapor deposition procedure shown on Figure 1. One percent water solution of Fe(NO₃)₃ with LiNO₃ in 1 and 10 of at. % regarding Fe and small quantity of HNO₃ was sprayed onto substrate heated at 593 K. The reaction is:

The home made apparatus for the preparation procedure was described previously [28].

The impedance measurements were performed using a homemade device consisting of an Impedance analyzer I-100 and sample holder with built-in thermocouple copper-constantan with cold junction compensator OMEGA-CJ. Measurements were performed in vacuum of 10^{-2} mbar. PC using software developed in our laboratory recorded the impedance response. Impedance spectra were measured in the frequency range from 100 KHz to 1 MHz. The samples (cubic-formed platelets consisting of Fe_2O_3 film on the glass substrate, with surface area of 100 mm^2 and 2.5 mm thickness) mounted between two zinc electrodes were placed in a spring-contacted apparatus compressing the cell between zinc/teflon cylinders. The idea was to measure glass substrate without Fe_2O_3 , and then with Fe_2O_3 films with different contents of Li. Measurements were consistent with model circuits [29], representing the sample/electrode systems as parallel sample resistance and capacitance in series with two impedances representing the electrode and sample characteristics.

TSC measurements were performed in the DL-4960 liquid nitrogen cryostat (Bio-Rad), using Keithley K-617 electrometer, under +10 V applied bias voltage, where contacts show ohmic behavior. Samples were heated in the dark until 360 K (in order to empty all deep traps/levels) and then cooled in dark to 85 K. After that, samples were illuminated with the white light during 600 seconds. Another fifty seconds samples were kept in the dark at 85 K and then temperature ramp with $\beta = 0.4 \text{ K/s}$ was activated. During that, regular TSC spectra were recorded.

Raman spectra were recorded using Dilor Z24 Raman triple monochromator in a 45° scattering configuration using 2 W of cylindrically focused 514.5 nm argon ion laser excitation. Micro-Raman spectra were recorded using Jobin Yvon T64000 in a backscattering configuration with objective LWD 50X of cylindrically focused 514.5 nm argon ion laser excitation.

The grain size, the crystallinity, and the morphology were observed using scanning field emission electron microscopy (SEM, Zeiss, Supra 35 VP).

The identification and classification of prepared samples were made by the X-ray diffraction using a D4 Endeavor, Bruker AXS.

3. Results and Discussion

The primary goal of impedance spectroscopy measurements was to determine the electrical conductivity of the Fe_2O_3 films and then Fe_2O_3 films with different contents of Li. Conductivity results were collected using Zn electrodes with continuous heating in a noninterrupted range between the room temperature of 295 K and 305 K. The conductivity values σ were calculated using the following equation:

$$\sigma = \frac{l}{SR} (\Omega\text{cm}^{-1}), \quad (2)$$

FIGURE 1: The Layout of the home made apparatus for CVD preparation of Fe_2O_3 thin films on glass substrate.

TABLE 1: Obtained parameters for different Fe_2O_3 samples: measurement temperature in degrees of K, resistivity R in $\text{k}\Omega\text{cm}$ obtained by IS, low-frequency Raman modes n in cm^{-1} , and their respective nanosizes d in nm of Fe_2O_3 films on the glass substrate.

sample	T/K	$R/\text{k}\Omega\text{cm}$	n/cm^{-1}	d/nm
Fe_2O_3	298	40	95	2.0
Fe_2O_3 with 1% Li	298	250	50	3.9
Fe_2O_3 with 10% Li	298	54	60	3.2

where l and S are the thickness and the area of samples, respectively. R is the sample resistance estimated from the ac admittance data, after fitting to the experimental curves.

Measurements with Zn electrodes were performed in impedance and admittance modes. Both measurements were performed because the bulk resistivity of the thin film of Fe_2O_3 , R_b , was more accurately determined from admittance, while charge transfer resistance, R_{ct} , was determined from impedance measurements.

Figure 2 is showing an example of ac admittance data for the sample of Fe_2O_3 obtained at room temperature and equivalent circuits.

At low temperatures, the geometrical capacity was neglected. Its typical values are rather low ($\sim \text{pF}$) deriving from a very high capacitive resistance in the C_g branch compared with the parallel R_b . So, the influence of C_g on the impedance on this parallel circuit can be neglected (Figure 2(b)).

We observed another arc at lower frequencies, which is attributed to a capacity between grain boundaries. By grains we assume crystallites divided by double layers between them. As R_{gb} was much bigger than R_b , its influence to the impedance circuit could be neglected so that only C_{gb} was left.

Figure 3 shows the conductivity plot in the range from 295 to 305 K for Fe_2O_3 and Fe_2O_3 : Li samples. Resistivities (R) obtained from admittance measurements at room temperature are shown in the second column of Table 1.

FIGURE 2: (a) Admittance spectra Fe_2O_3 thin film measured at room temperature and (b) equivalent circuits and schematic admittance plot for Zn electrodes.

FIGURE 3: Log σ versus $1000/T$ for Fe_2O_3 (1), Fe_2O_3 with 1% (2) and Fe_2O_3 with 10% of Li (3) measured with Zn electrodes.

Figure 4. shows TSC spectra of three Fe_2O_3 samples with different Li content, e.a. pure Fe_2O_3 (0% Li), with 1% and finally with 10% of Li, respectively. This figure, showing (a) low- and (b) high-temperature regions, illustrates changes in the defect concentrations related to the different Li contents. Low-temperature TSC spectra are characterized by the negative peak around 155 K, related to the deep trap T_2 (with activation energy, $E_a = 0.28$ eV) and calculated by equation [25]:

$$E_a = kT_m \ln \left(\frac{T_m^4}{\beta} \right), \quad (3)$$

where k is the Boltzman's constant, T_m is temperature of TSC peak maximum (in K), and β is heating rate in K/s. It was observed in Fe_2O_3 Li-free samples and in TSC of Fe_2O_3 with 1% Li. According to the literature [30, 31], we assign our

TABLE 2: Main parameters of deep traps found in Fe_2O_3 samples.

Trap	T_1	T_2	T_3	T_4	T_5
E_a (eV)	0.18	0.28	0.36	0.64	0.68
T_m (K)	107	155	188	308	327

peak T_2 to the hole trap. Two neighboring peaks, T_1 (with $T_m = 107$ K and $E_a = 0.18$ eV) as well as T_3 (at 188 K, 0.36 eV) should correspond to electron traps. TSC spectrum of the sample with 10% Li shows the increase of T_1 and T_3 concentrations, which “screened” negative peak T_2 . It can be explained by abundant release of oppositely charged carriers—electrons from T_1 and T_3 traps and/or by the decrease of the holes traps concentration caused by the structural changes after Li entered into the structure. It should be noticed that doping with 1% of Li causes increase in T_2 hole trap concentration, while further doping (10%) increases T_1 and T_3 peaks. The same observation can be applied for TSC peaks in high-T region. Namely, peaks T_4 (at 308 K, 0.64 eV) and T_5 (327 K, 0.68 eV) decrease in samples with 1% Li and enormously increase in samples with 10% Li content. Main deep trap parameters are presented in Table 2.

In this work, we have determined nanosized values for the acoustic phonons in Fe_2O_3 by using the method of low-frequency Raman scattering that had been tested on different powder systems in our previous work [32]. Generally, this method is based on the work of Duval et al. [33], who showed that the maximum of the low-frequency mode of a free particles, n , corresponds to the angular momentum $l = 0$ and it is given by

$$n = 0.7(v_l/(d \cdot c)), \quad (4)$$

where c is the velocity of light in vacuum, v_l is the longitudinal velocity of sound, and d is particle diameter. In calculations, we have used $v_l = 8300$ m/s of $\alpha\text{-Fe}_2\text{O}_3$ [34].

FIGURE 4: TSC spectra of (a) low- and (b) high-temperature region of three samples with different Li content, e.a. Fe₂O₃ (Li free), Fe₂O₃ with 1% and Fe₂O₃ with 10% of Li.

The results of calculations are presented in Table 1. Raman spectra, measured at room temperature and used in Fe₂O₃ nanosizes determination, are shown at Figure 5. Average nanosizes in sample with 1% of Li increased regarding to the original Li free sample from 2.0 nm to 3.9 nm. After addition of 10% of Li, nanosizes were reduced to 3.2 nm.

We have performed assignation of Raman lines according to the literature [35–38] as hematite and it is shown in Table 3. Hematite, α -Fe₂O₃ with corundum structure belongs to the D_{3d}^6 crystal space group, which gives seven characteristic phonon lines $2A_{1g} + 5E_g$ that are Raman-active fundamentals. Additional Raman experiments were performed after period of 8 months showing stability of hematite phase. Shift of the Raman lines towards higher frequencies upon insertion of Li⁺-ions into the structure is also showing nanostructured [39, 40] nature of the films.

In further discussion, we will try to correlate the results of three types of measurements (IS, TSC [25], and Raman) in

order to gain insight in microscopic resistivity increase upon addition of Li.

Charge transport in simple 3d oxide crystals such as α -Fe₂O₃ can be described in terms of hopping and narrow-band conduction by polarons [41]. The electron transition in α -Fe₂O₃ usually occurs between the partially filled 3d orbital and the nearly empty sp orbital of O. In a narrow band semiconductors like α -Fe₂O₃, disorder may produce localized states in the whole band. The disorder potential between adjacent states is [41]

$$W_D \geq 6(2Jz), \quad (5)$$

where J is the overlap integral between 3d orbitals and z the number of nearest neighbours. In this case, conduction takes place by phonon-assisted hopping of electrons.

The polaron theory that is in detail presented in [41] is one of the possible approaches to interpret our data. Here we introduce view of nanosized acoustic phonons in Raman spectra as quasiparticles, when coupled to the electron, that is, nanoparticle. Low-frequency Raman showed that adding of 1% Li induced significant changes in the nanoparticle size (2 nm $\rightarrow$ 3.9 nm), which is the increase of 95%, and accordingly in the conduction mechanism. Li⁺ ions affected holes traps as determined by TSC [25] by increasing their concentration, while electron traps concentration decreased. Activation energies of electrons' and holes' traps $T_1 - T_5$ remained almost the same (0.18, 0.28, 0.36, 0.64, and 0.68 eV), respectively [25]. One possible explanation is that Li⁺ ions combined with related defects in the unit cell causing decrease of overlap integrals and accordingly decrease in the disorder potential W_D . This induced tensions in the structure that resulted by the nanoparticle enlargement and accordingly its mobility decreases. Increase in resistivity for more than six times was observed (Table 1). The situation is quite different in samples with 10% Li: nanoparticle size decreased from 3.9 nm to 3.2 nm and resistivity simultaneously decreased almost to the value of the referent Li free sample. The increase of the conductivity is due to structural disorder created by Li⁺ ions, which are having ten times greater concentration than in the sample with 1% Li. In such disordered structure, disorder potential can vanish and nanoparticle can easily move through the sample. The mechanism of hopping electrons can also occur and add to the conductivity increase. The same observation can be applied for TSC peaks in high- T region, namely, peaks T_4 (at 308 K, 0.64 eV) and T_5 (327 K, 0.68 eV) decrease in samples with 1% Li and enormously increase in samples with 10% Li [25]. These two peaks represent deep traps and as they decrease upon addition of 1% of Li, the conductivity also decreases, which is in agreement with IS measurements (Table 1). Further increase of Li content to 10% increases concentrations of these traps and conductivity increases, due to enlarged release of electrons from traps, which is also in accordance with IS results. The increase in deep traps concentrations indicates that samples with 10% Li are amorphous.

Scanning field emission electron microscopy and XRD measurements were performed in order to check the grain size, the crystallinity, and the morphology, revealed by other methods.

TABLE 3: Raman wave numbers and assignments of the hematite films prior and after addition of Li^+ ions.

Assignment	Raman shift/ cm^{-1}					
	1			2		
	Fe_2O_3	$\text{Fe}_2\text{O}_3 + 1\% \text{ Li}$	$\text{Fe}_2\text{O}_3 + 10\% \text{ Li}$	Fe_2O_3	$\text{Fe}_2\text{O}_3 + 1\% \text{ Li}$	$\text{Fe}_2\text{O}_3 + 10\% \text{ Li}$
	78 w	56 sh	69 vw			
	99 sh					
A1g(1)	213 vs	221 w	221 m	223 s	223 sh	219 vw
Eg(1)				241 sh	245 w	241 vw
				267 sh		
Eg(1)	282 vs	286 vs	284 m	290 vs	297 m	296 m
Eg(1)	395 w	402 vs	393 s	404 s	407 vs	407 s
A1g(2)		488 w	490 w	490 vw		
Eg(1)	586 w	608 w	600 w	608 w	609 w	608 w

1: First measurement, 2: Second measurement after 8 months: vs: very strong, s: strong, m: medium, sh: shoulder, w: weak, vw: very weak.

FIGURE 5: Raman spectra of Li free Fe_2O_3 (1), Fe_2O_3 with 1% (2), and Fe_2O_3 with 10% of Li (3). Inset shows low-frequency region of the same spectra pointing out low frequency modes revealing nanosizes.

SEM photographs of $\alpha\text{-Fe}_2\text{O}_3$ and of the same material with added Li ions are shown on Figure 6. It is clearly visible on lower magnification that sample (a) shows much more homogeneous surface than the samples (c) and (e). The crystallinity is changed and films (c) and (e) became partly and completely amorphous, respectively. The surface of sample (e) shows good homogeneity and on higher

magnification some nanoagglomerated grains are visible. Figures 6(b), 6(d), and 6(f) present SEM photographs of the same films after 8 months, demonstrating no significant difference upon earlier results.

On higher magnification in Figure 7, it is shown that film Fe_2O_3 is formed from nanograins in the radius, R , range from 75 nm to 240 nm. The maximum for grain size distribution

FIGURE 6: SEM photographs Li free Fe_2O_3 (a), Fe_2O_3 with 1% (c) and Fe_2O_3 with 10% of Li (e), and the same films after 8 months (b), (d), and (f), respectively.

is at $R = 120$ nm as fitted to Lorentian shape. It is confirmed that the grains are crystalline as shown on XRD spectra shown on Figure 8. The tensions in the crystalline structure are seen as cracks in Figure 7.

The results of the XRD measurements of the samples prepared as films on the glass substrate are presented on Figure 8. The prepared film on Figure 8(a) showed the characteristic diffractogram of hematite structure (reference code 01-079-1741, mineral name: Hematite, synthetic, ICSD name: Iron Oxide).

We have calculated grain sizes in Fe_2O_3 by using Debye-Scherrer formula:

$$D = \frac{0.9 \cdot \lambda}{\beta \cos \theta}, \quad (6)$$

where D is diameter of grain, λ is the wavelength of the X-ray beam, β is the width at the half height of the particular

line in radians, and $\cos \theta$ is the position of the peak in 2θ scale. D values were obtained in the range from 20 nm to 110 nm, which is in agreement with the nanometre range of grain sizes observed on SEM photograph shown in Figure 7.

At Figure 8(b), only one small intensity peak at 39.295° with $D = 27$ nm is shown. The recordings were with the same intensity (see y -axes) as in Figure 8(a). Figure 8(c) is not showing any crystalline lines. Figure 8 clearly shows amorphization of the sample upon addition of Li^+ ions, from pure crystalline hematite (a), through amorphous phase with 1% Li (b) and to completely amorphous phase with 10% Li (c).

4. Conclusion

As a conclusion, the present study showed that IS, Raman spectroscopy, SEM, and XRD could be applied for grain

FIGURE 7: SEM photograph Li free Fe_2O_3 (a), with higher magnification of 100.00 K.

FIGURE 8: XRD spectra of Fe_2O_3 (a), Fe_2O_3 with 1% (b), and Fe_2O_3 with 10% of Li (c).

size and conductivity determination in nanosized films of Fe_2O_3 and Fe_2O_3 : Li on glass substrate. The results obtained with IS, Raman spectroscopy and previously, with TSC analysis [25], together with XRD and SEM give complementary data to build a model of the charge transport in these nanostructured films. IS revealed trends in conductivity changes, while TSC gave insight in deep traps concentration changes related to the increase of Li percentage in Fe_2O_3 . By the low-frequency Raman spectroscopy, it was possible to follow changes of the nanoparticles (which are acoustic phonons

coupled to electrons with the nanosize diameter range $d < 5$ nm), during the structural changes induced by the introduction of Li into the Fe_2O_3 . It was observed that nanoparticles sizes are increasing with addition of Li to the films, and a little bit decreasing with further increase of Li content. Also, Raman spectroscopy showed that we were dealing with nanostructured α - Fe_2O_3 (hematite) films. Samples also showed steadiness, during rest period of eight months. XRD measurements additionally proved that samples are α - Fe_2O_3 , hematite phase of iron oxide. SEM patterns, as well as Raman and XRD, showed that the addition of Li^+ ions have changed nanostructure of the samples from the crystalline grains in the diameter range $D > 20$ nm to the amorphous phase.

Here we point out the distinction between the two terms, nanoparticles and nanograins, used in this paper, as they are describing noncrystalline and crystalline forms, respectively. Nanoparticles could be possibly seen as seeds for the amorphization process during the increase of Li percentage in our samples.

This particular morphology is suitable for application in an advanced electrochemical cell concept, which could be used as charge storage for solar cells.

Acknowledgments

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