Structural and Electrical properties of PVDF doping lithium Iron Oxide nano-composites

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Abstract
Lithium iron oxide, LiFeO$_2$ (LFO) powder has been successfully prepared by Sol-Gel process. The structure, electrical and dielectric properties were investigated, cubic structure for LFO was characterized by X-ray diffraction (XRD). PVDF polymer was added to the LFO is prepare composites with different percentages (1, 2, 3 and 4) wt.%. The results show that A.C. conductivity depending frequency shows an increasing in value depending on the mobility of carrier and the dielectric properties. A.C. conductivity shows the expression for the mobility of charge carriers, this study shows the effect of filler relation with PVDF which effect the mobility of polymer chain, this behaviour used to analyse the dielectric response of oxide.

Key Words: PVDF, LFO, dielectric properties, Cole-Cole, Sol-gel.

Introduction
In view of the structural properties of the ceramic semiconductor nanoparticles, the researchers mainly focused on treating and synthesizing them in different ways, specifying and applying them widely in many technological fields. When a ceramic material minimizes to the nanoscale level, a severe change in chemical and physical properties is realized and due to the large surface area, it is really helpful for technological purposes [1].
LiFeO$_2$ (LFO) has been presented in various crystalline forms, which is a major constraint of lithium minerals as electrode materials due to the low cycling efficiency and low operating voltage. Iron-based compound has given much attentiveness as effective matotrials for Lithium rechargeable batteries. LiFeO$_2$ has several structural phases, like $\alpha$-, $\beta$- and $\gamma$-conjugated forms. LiFeO$_2$ has important advantages such as it is non-noxious, holds the common abundant and cheap metal available in the world. It is used in wide fields such as cathode material in “lithium ion batteries” [2].

PVDF ( -CH$_2$-CF$_2$-)$_n$ shows four crystalline polymorphs structures including the $\alpha$-, $\beta$-, $\gamma$- and $\delta$- phases depending on different processing techniques. PVDF, a dielectric polymer, has been investigated because of its excellent characteristics such as a good piezoelectric/pyroelectric response, chemical resistance and high dielectric permittivity, so that it can be formed in a variety of nano-structures, such as nano-wire, nano-fiber and nano-tube. Because of PVDF is polymorphic semi-crystalline polymer that preforms in different crystalline forms, nanoparticles can have an effect on morphological form, as well as crystalline on the crystallization of the semi-crystalline polymer in addition to changing the effective properties [3-5].

2. Experimental Techniques

Synthesis of LiFeO$_2$ powder was processed by “chemical Sol-gel method”. Firstly, using equal amounts nitrates of (Li and Fe) with “citric acid” unerased & mixed with “DI water”, and leave the mixture for 1 day in “70°C” to let it evaporate until it gets gelled, then heat-treated at (650°C) for two hours.

3. RESULTS and DISCUSSION

A. X-ray Diffraction Analysis
The X-ray diffraction (XRD) pattern for LiFeO$_2$ synthesis by the Sol-gel method is described in Fig 1. It has shown Crystalline peaks of powder sample were identified for LiFeO$_2$ (LFO) which indicates the formation of cubic (JCPDS NO. 96-100-8637), corresponding to the planes (111), (311), (222), (400), (440), (622), (444) and (800). And table 1 explained the structural properties (FWHM, index plane and grain size). Some extra secondary peaks (Fe$_2$O$_3$ secondary phases) are seen adjacent to characteristics peak and perhaps due indicates the existence of the impurity phase attributed of LiFeO$_2$ are the limiting segments of the solid solutions created by the replacement of Fe$^{2+}$ by Li+Fe$^{3+}$ in Fe$_3$O$_4$, calcination free phase transform show a transform a hematite $\alpha$-Fe$_2$O$_3$ to magnetite Fe$_3$O$_4$ and LiFeO$_2$ by reduction of Fe$^{3+}$ ion to Fe$^{2+}$[4][6].

![X-ray diffraction spectra of LiFeO$_2$](image)

Fig. 1 : X-ray diffraction spectra of LiFeO$_2$

Table 1 : the structural properties of LiFeO$_2$ and Fe$_3$O$_4$ powder
### B. Electrical properties

The measurement of A.C electrical conductivity ($\sigma_{a.c}$), the A.C. results explained the conductivity behaviour of oxide addition to PVDF, it has shown that the reaction decreased with oxide addition (LFO), depend on “frequency” range as a parameter to determine the optimal frequency and capacitance as a parameter used in assessment of behaviour of these nano-composite to “electrical conduction”.

The capacitance’s variation with angular frequency for pure PVDF, and PVDF doped LiFeO$_2$ with different ratio (1%, 2%, 3%, and 4%) wt. It can be shown in Fig. 2, that the capacitance of the composites decreases with increasing content of LFO doped, the reaction of these material (PVDF) was decrease due to the differing in weight of added oxides.

| 20 (Deg.) | FWHM (Deg.) | $d_{hkl}$ Exp.(Å) | G.S (nm) | $d_{hkl}$ Std.(Å) | Phase | hkl | card No. |
|-----------|-------------|------------------|---------|-----------------|-------|-----|---------|
| 18.3734   | 0.2848      | 4.8249           | 28.3    | 4.8685          | Cub.LiFeO$_2$  | (111) | 96-100-8637 |
| 35.5759   | 0.3987      | 2.5215           | 20.9    | 2.5425          | Cub.LiFeO$_2$  | (311) | 96-100-8637 |
| 36.8291   | 0.4557      | 2.4385           | 18.4    | 2.4343          | Cub.LiFeO$_2$  | (222) | 96-100-8637 |
| 42.9241   | 0.4557      | 2.1053           | 18.7    | 2.1081          | Cub.LiFeO$_2$  | (400) | 96-100-8637 |
| 43.9494   | 0.3987      | 2.0585           | 21.5    | 2.0535          | Cub.Fe$_3$O$_4$ | (400) | 96-900-2327 |
| 48.2785   | 0.6266      | 1.8836           | 13.9    | 1.8844          | Cub.Fe$_3$O$_4$ | (331) | 96-900-2327 |
| 58.3608   | 0.5127      | 1.5799           | 17.7    | 1.5808          | Cub.Fe$_3$O$_4$ | (333) | 96-900-2327 |
| 62.5190   | 0.7405      | 1.4844           | 12.6    | 1.4907          | Cub.LiFeO$_2$  | (440) | 96-100-8637 |
| 74.9937   | 0.5696      | 1.2654           | 17.6    | 1.2712          | Cub.LiFeO$_2$  | (622) | 96-100-8637 |
| 75.7911   | 0.5696      | 1.2541           | 17.7    | 1.2526          | Cub.Fe$_3$O$_4$ | (533) | 96-900-2327 |
| 79.0949   | 0.7974      | 1.2098           | 12.9    | 1.2171          | Cub.LiFeO$_2$  | (444) | 96-100-8637 |
| 92.3671   | 0.5697      | 1.0675           | 20.1    | 1.0694          | Cub.Fe$_3$O$_4$ | (553) | 96-900-2327 |
| 94.8734   | 1.0253      | 1.0458           | 11.5    | 1.0541          | Cub.LiFeO$_2$  | (800) | 96-100-8637 |
| 97.8924   | 0.6266      | 1.0215           | 19.3    | 1.0267          | Cub.Fe$_3$O$_4$ | (800) | 96-900-2327 |
Figure (2): Variation of capacitance (C) with frequency for pure PVDF, and PVDF doped LiFeO$_2$

Figure (3): Variation of A.C conductivity with frequency for pure PVDF, and PVDF doped LiFeO$_2$
Fig. 3. Reaction rate between “PVDF” and LiFeO$_2$ doped with different ratio (1%, 2%, 3%, and 4%) wt. are shown. The $\sigma_{\text{a.c}}(\omega)$ for all samples has observed to increase with increasing frequency. The variations of dielectric constant, real part ($\varepsilon_1$) and imaginary parts ($\varepsilon_2$), with frequency are described for various concentration of PVDF, and PVDF:LiFeO$_2$ doped with different ratio (1%, 2%, 3% and 4%) wt. have be shown in Fig. 4 (a and b). These results observations prove that the electric properties of the polymer improve by adding LFO, and it is indicated that the entered ceramic fillers and interface areas have positive impacts on the structure of the polymer matrix and contribute to the enhancement of the dielectric responses and energy storage properties of the nano-composites [8]. That is cleared that the real part ($\varepsilon_1$) decrease with the increase in frequency, the high value of $\varepsilon_1$ at low frequency was attributed to existed. It is observed from Fig. 4, that the magnitude of dielectric loss decreases with increase of frequencies. The dielectric constant decreased gradually due to the enhancement of the mobility charge carrier; this behaviour is for polar dielectric material. The dielectric relaxation is a result of dipoles in metal-ion chains which shows a peak in $\varepsilon_2$ spectra [9].

The role of addition of LiFeO$_2$ with different percentage is to increase the electric behavior of nano-composite and so on increase the conductivity due to the formation of nano-crystalline porous environmentally friendly cathode for Li-ion battery.

The decreasing in the grain size decreasing the volume and increasing the mobility of lithium ions because it offers conductive path ways along the structure as a way to transport of electrons.
Figure (4): Variation of dielectric constant a) real part ($\varepsilon_1$) and b) imaginary part ($\varepsilon_2$) with frequency for pure PVDF, and PVDF doped LiFeO$_2$

The “Cole-Cole” plots in materials with multiple relaxation process will be semicircles with centres below the real axis. The semi-circular Cole-Cole plots for different percentages of LFO: PVDF (1%, 2%, 3%, and 4%) wt. is given in Fig. 6. The semicircles drawn are the simulated ones and the curved line the experimental one.

The imaginary part of dielectric constant is a pattern of energy spent during the polarization. As the amount of LFO increases, the dipoles can simply
arrange with the field and so the maximum value of the imaginary part of dielectric constant decreases.

The “Cole-Cole” plot in the material ($\varepsilon_2$ vs $\varepsilon_1$) is a tool that used to holding materials one or more than one well detached relaxation operation, with analogous magnitudes, it will be semicircles with centres below the real axis. The plot includes the variation of the loss of dielectric with the storage of dielectric element at fixed temperature and figuration of typical semi-circle show the behaviour of single relaxation time [9].

Semi-circular arc depression due to wide relaxation zone has been shown in Fig. 5, and its highest loss happens at the midpoint of the curve, whereas the dielectric value is recorded from right to left with frequency increasing. while the dielectric value is read form right to left with an increase of frequency. Once exciting conclusion is noted, that the loss occurs at a dielectric constant of infinite frequency ($\varepsilon\infty$) and static dielectric constant ($\varepsilon_s$).
Fig. 6: Cole-Cole diagram of PVDF: LFO with different percentage

Conclusion:
Lithium iron oxide has been successfully prepared by sol-gel. The crystalline of powder behave as electrical conductance. The addition of nano-crystalline LiFeO$_2$ powder to PVDF polymer enhanced the electrical properties due to electron transfer in the nano-composites, the polymer prevents the formation of crack in the electrode during the charge-discharge process and act as conducting matrix and protective coaling.
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