Impact of Incorporating Different Metal Oxide Nanoparticles on Structures and AC Conductivity of PVC/PVDF-based Electrolytes

Russul A. Hasson
Ahmad A. Hasan

Department of Physics,
College of Science,
University of Baghdad,
Baghdad, IRAQ

Iraqi Journal of Applied Physics
Q4 Electronic, Optical and Magnetic Materials
best quartile
SJR 2022
0.19
powered by scimagojr.com

The synthesis of metal oxide nanoparticles-doped PVC/PVDF/LiCl and PVC/PVDF/Li$_2$CO$_3$, plasticized with glycerol, was carried out. The solid polymer electrolyte (SPE) was analyzed for its structural properties and ionic conductivity using X-ray diffraction and an LCR meter. The structural analysis revealed that the SPE possessed a semi crystalline structure. The use of lithium salts resulted in a reduction in crystallinity or a transition towards an amorphous phase. However, the inclusion of metal oxide NPS led to an increase in the broadening of the most dominant diffraction peaks. The A.C. conductivity measurements demonstrated that the highest conductivity was achieved in PVC/PVDF/LiCl doped with WO$_3$NPs. Measurements were conducted for both the dielectric constant and the dielectric loss. The minimal glass transition temperature for PVC/PVDF/LiCl doped with WO$_3$NPs was determined using differential scanning calorimetry.

Keywords: Metal oxides; Glycerol; Solid polymer electrolytes; Nanoparticles; XRD
Received: 31 October 2023; **Revised:** 05 December; **Accepted:** 12 November 2023

1. Introduction

Since the commercialization of lithium-ion batteries (LIBs) with a liquid electrolyte in the 1990s, LIB development has achieved incredible achievements, profoundly altering people's daily lives [1,2]. Lower explosion risk, improved electrochemical stability, and the absence of leakage [3] are just a few of the benefits that solid-state electrolytes offer over their liquid version. Poly (vinyl chloride) (PVC), a thermoplastic polymer, has a global fabrication demand second only to polypropylene [4]. Poly(vinylidene) fluoride (PVDF), a thermoplastic polymer with strong electrochemical stability, is commonly used in electrical and battery applications [5,6]. Lithium salts, a preferred choice due to their superior dissociation, are used in electrolytes due to their role in conductivity, electrochemical, thermal, and mechanical stability. Inorganic nanofillers, which prevent polymer matrix crystallization, improve ionic conductivity by preventing crystallization [7,8].

In this study, glycerol is used as a plasticizer to enhance the flexibility of the polymer matrix consisting of 80% PVDF and 20% PVC. Various salts, including lithium carbonate and lithium chloride, along with three metal oxides (copper oxide, tungsten trioxide, and titanium dioxide), were employed as fillers within a PVDF/PVC matrix. An investigation was conducted to examine their impact on the structure and A.C. conductivity.

2. Experimental Part

The main chemicals are PVDF and PVC. LiCl, Li$_2$CO$_3$, CuO NPs, WO$_3$ NPs, TiO$_2$ NPs, glycerol, and the solvent Tetra-hydrofuran (THF) were provided by Sigma-Aldrich. The electrolyte-thin films were created via solution casting. A solution was prepared by dissolving 20% of PVC and 80% of PVDF in THF. Subsequently, a solution mixture was supplemented with 10% LiCl, 0.01% filler, and 3 ml of plasticizer. The solution was stirred using a magnetic stirrer to ensure homogeneity. Afterward, the solution was transferred to a petri dish, and the solvent was left to evaporate at room temperature. The thickness of the freestanding films was determined using a digital micrometer, giving a measurement of 0.03 mm. In order to completely remove any remnants of THF, the electrolytes underwent vacuum drying. The Li$_2$CO$_3$ salt was used in comparable research utilizing the identical approach. The XRD measurements were conducted using the PANalytical X'Pert PRO XRD instrument with Cu Kα radiation. AC measurements were conducted using an LCR meter, which included dielectric and conductivity measurements performed at ambient temperature. The AC conductivity provides insight into the electronic conductivity of the material, the interface between the electrodes and the capacitance, as well as the processes related to dielectric polarization. This phenomenon is observed in the amorphous, nonmetallic state, likely because of the movement of electrons or ions, which can occur by hopping or tunneling between equilibrium states. The total conductivity σ_{tot} (ω) at a certain frequency and temperature is defined as [9]:

$$\sigma_{tot} = \sigma_{a.c}(\omega) + \sigma_{d.c} \quad \text{or}$$

$$\sigma_{tot} = A\omega^{s} + \sigma_{d.c} \qquad (1)$$

where $\sigma_{d.c}$ is the D.C. conductivity, which depends strongly on temperature and dominates at low frequencies, while $\sigma_{a.c}$ is the A.C. conductivity, which has weaker temperature dependence than $\sigma_{d.c}$ and dominates at high frequencies and nondependent temperatures. and (s) is a function of frequency and is determined from the slope of a plot ln $\sigma_{a.c}$ (ω) versus ln (ω)

A.C. conductivity across a wide frequency range can be obtained using the formula [10]:

$$\sigma_{tot} = \frac{t}{R.A} \qquad (2)$$

where t is film thickness, A is effective capacitance area, and R is resistance. Consider the formula below to calculate the dielectric constants (ε_r, ε_i):

$$\varepsilon_r = \frac{C.t}{\varepsilon_o\, \omega} \qquad (3)$$

$$\varepsilon_i = \frac{t}{\omega\, \varepsilon_o\, RA} = \frac{\sigma_{a.c}}{\varepsilon_o\, \omega} \qquad (4)$$

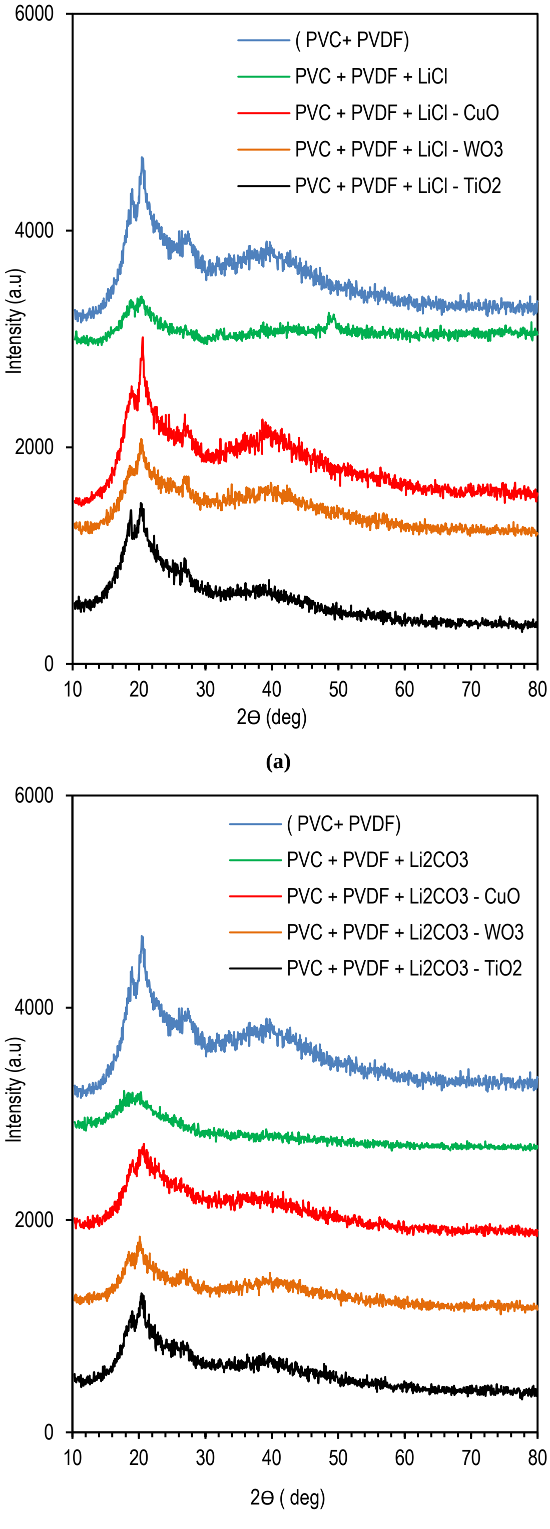
where C is the capacitance and ε_o is the permittivity of free space = 8.854×10^{-14} F/cm.

3. Results and Discussion

The semi-crystalline nature of PVC/PVDF mixes arises from the disruption of PVDF's long-range order by PVC. The PVC/PVDF blend exhibited peaks at 2θ equals to 18.6923°, 20.5828°, and 24.2978°. The PVC/PVDF/LiCl, Li_2CO_3 blends exhibit a higher degree of amorphousness compared to the PVC/PVDF mix, mostly attributed to their less crystalline structure and presence of significant voids [11]. The decreased peak intensities seen in the PVC/PVDF/LiCl/CuO mix indicate that the presence of cation complexes with the functional group of the PVC/PVDF blend has expanded the size of the amorphous region. These results indicate that nanoparticles have successfully entered the PVC/PVDF polymer system.

According to Hodge et al. [12], there is a correlation between peak intensity and crystallinity. Therefore, this relationship can be interpreted in that manner. The XRD examination revealed that the PVC/PVDF mix had a 2θ value of 18.6923°, but the PVC/PVDF/LiCl, Li_2CO_3/WO_3 blends were missing this value. The addition of fillers resulted in an expansion in the width of the peaks observed in the doped sample, as shown in Fig. (1). Consequently, the phenomenon of peak broadening indicates the emergence of amorphous components in the samples. The increase in conductivity has been demonstrated to be directly correlated with the amorphous nature of the material.

Figure (2) illustrates the relationship between angular frequency and total conductivity σ_t (ω) for PVC/PVDF/LiCl, Li_2CO_3 blends, both undoped and doped with metal oxide nanoparticles. The study demonstrates that σ_t (ω) experiences a modest rise in the low-frequency range as a result of interfacial polarization, hence reducing its dependence on frequency. The presence of charge carriers between the valence and conduction band extremities leads to substantial D.C. conductivity.

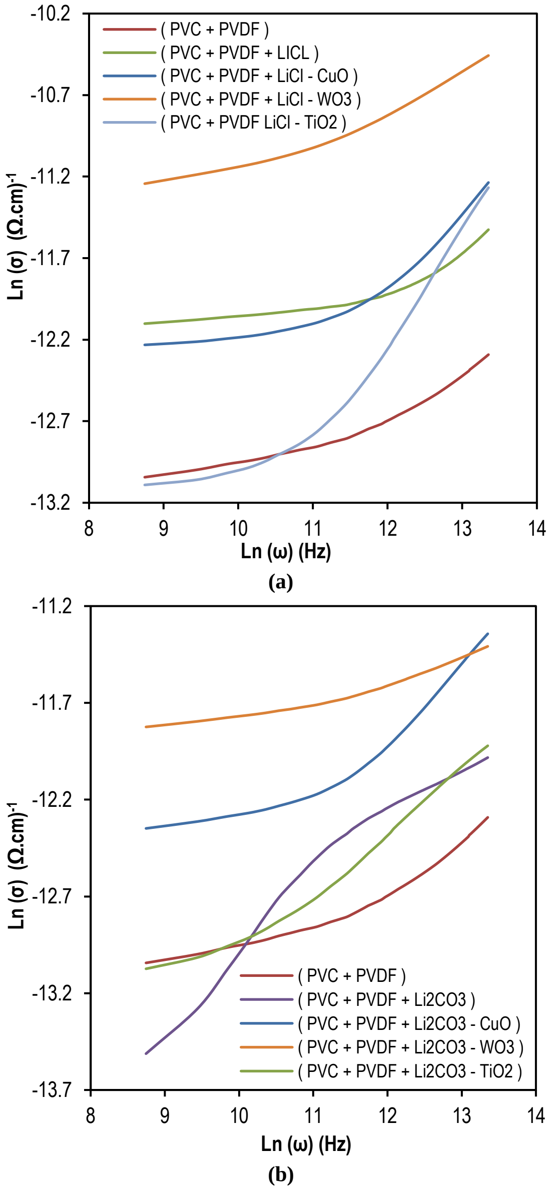


(a)

(b)

Fig. (1) XRD patterns for undoped and doped PVC/PVDF/LiCl blends (a) and PVC/PVDF/Li_2CO_3 blends (b) with metal oxides

The conductivity, denoted as σ_t (ω), shows a rapid increase in the higher frequency range, indicating electronic polarization. In this range, the conductivity is purely alternating current. Equation (1) states that if σ_{dc} is significantly smaller than the second term at a given temperature, then σ (ω) is proportional to ω^s. Consequently, the plot of Ln (σ) versus ω will have a linear relationship with a slope of s. The PVC/PVDF exhibited an "*S*" value of 0.2128. The fact that the s values are smaller than one verifies the presence of the hopping mechanism [13]. The addition of LiCl causes a reduction in s to 0.1712, while the addition of Li_2CO_3 leads to an increase in *S* to 0.2628. Therefore, the most appropriate model is correlated barrier hopping (CBH), and the most acceptable model is small polaron.



(a)

(b)

Fig. (2) Variation of Ln (σ_{ac}) (ω) with Ln (ω) of undoped and doped PVC/PVDF/LiCl blends (a) and PVC/PVDF/Li_2CO_3 blends (b)

The CBH model is utilized when electrons traverse the potential barrier between two sites. The A.C. conductivity arises from the hopping of electrons between defect states or dangling bonds (D^+D^-). Exponent s rises when the addition of the charge carrier to the covalent solid induces significant local lattice deformation, resulting in the formation of a small polaron [14] by the doping effect with CuO, WO_3, and TiO_2 [15-18]. The value of s increases in a non-regular sequence to 0.3185, 0.2208, and 0.5829 for PVC/PVDF/LiCl blends and to 0.3165, 0.1171, and 0.3216 for PVC/PVDF/Li_2CO_3 blends. The increased mobility of charge carriers in the composite film led to a conductivity of 9.88×10^{-6} S/cm for the PVC/PVDF/LiCl and 6.25×10^{-6} S/cm for the PVC/PVDF/Li_2CO_3 at a frequency of 100 kHz. CuO nanoparticles exhibited strong interactions with polymer chains, facilitating unhindered ion mobility. This enhances the movement of ions [19,20]. Figure (2) shows higher ionic conductivity measurements of 1.32×10^{-5} S/cm for PVC/PVDF/LiCl/CuO and 1.19×10^{-5} S/cm for PVC/PVDF/Li_2CO_3/CuO due to the presence of stronger forces acting on the ions, resulting in faster movement. TiO_2 and WO_3 nanoparticles facilitated ion transport within the polymer electrolyte by establishing channels. Consequently, the increase in frequency resulted in enhanced ion mobility and accelerated ion diffusion due to the availability of additional pathways for ion movement. The improved ionic conductivity can be due to increased ion diffusion, resulting in values of 1.28×10^{-5} S/cm for PVC/PVDF/LiCl/TiO_2 and 6.64×10^{-6} S/cm for PVC/PVDF/Li_2CO_3/TiO_2 blend [21,22]. The PVC/PVDF/LiCl/WO_3 blend exhibited a maximum ionic conductivity of 2.87×10^{-5} S/cm, whereas the PVC/PVDF/Li_2CO_3/WO_3 achieved a conductivity of 1.11×10^{-5} S/cm.

The dielectric constant ε_r of PVC/PVDF/LiCl, Li_2CO_3 were determined by measuring it with three different types of metal oxide nanoparticles, as shown in Fig. (3). The findings indicated that the introduction of lithium chloride led to an increase in ε_r, but an increase in frequency resulted in a decrease in ε_r due to electrode polarization. The influence on dielectric behavior [23] can be attributed to the dominant electrode blocking layer. The incorporation of various metal oxides had a significant impact on the ε_r values. Specifically, at a frequency of 10 kHz, the dielectric constant grew from 10454 to 25000. However, doping with WO_3 resulted in a fall in the dielectric constant to 8.7, while doping with TiO_2 also led to a decrease. In materials that have different phases or components, charge carriers can become trapped and build up at the boundaries between these phases and at defects. This accumulation of charge leads to the distortion of an electric field and an increase in the dielectric constant.

The phenomenon in question is referred to as the Maxwell-Wagner effect, and it is dependent upon the conductivity of the existing phases. Decreasing the total polarization of the material leads to a reduction in the value of ε_r. The ionic conductivity demonstrates that the increased bulk and limited mobility of ions can hinder the migration of the polymer matrix. Decreased ionic mobility contributes to a reduction in ε_r [24,25]. As the frequency of the applied electric field increases, the imaginary dielectric constant of polymer electrolytes falls. This is attributed to restrictions in ion mobility and relaxation processes, as illustrated in Fig. (4). The imaginary dielectric constant is also influenced by the interactions of polymers and electrolytes with other substances or phases. High frequencies can amplify interfacial phenomena, leading to alterations in the imaginary dielectric constant. CuO and WO_3, are polar materials with large dielectric constants. Conversely, TiO_2 is incorporated as a filler into a polymer electrolyte, augmenting its dielectric constant.

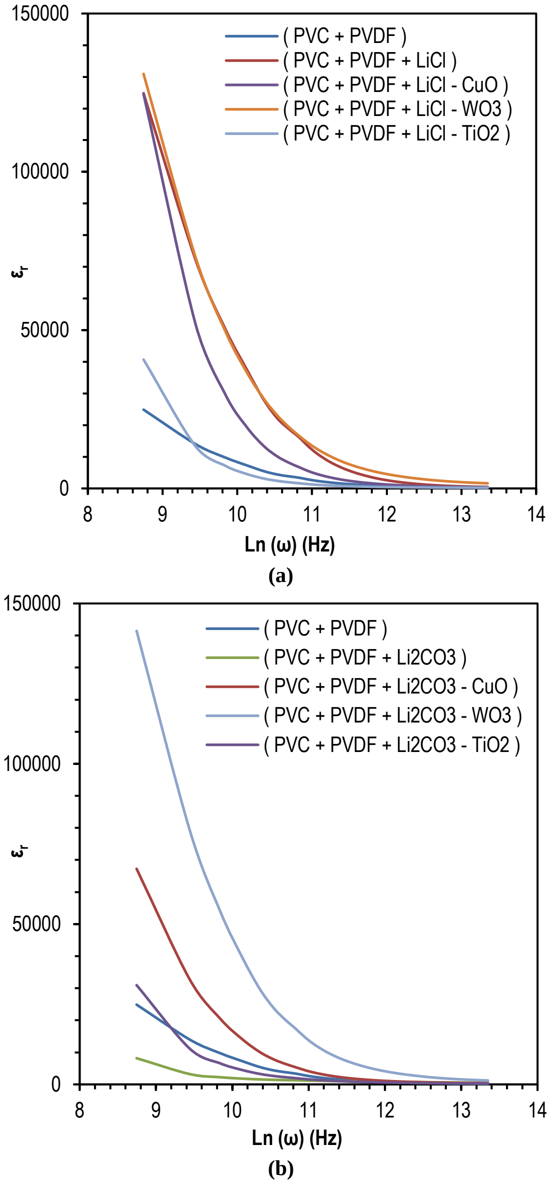


Fig. (3) Real dielectric constant as function of Ln (ω) for undoped and doped PVC/PVDF/LiCl blends (a) and PVC/PVDF/Li_2CO_3 blends (b)

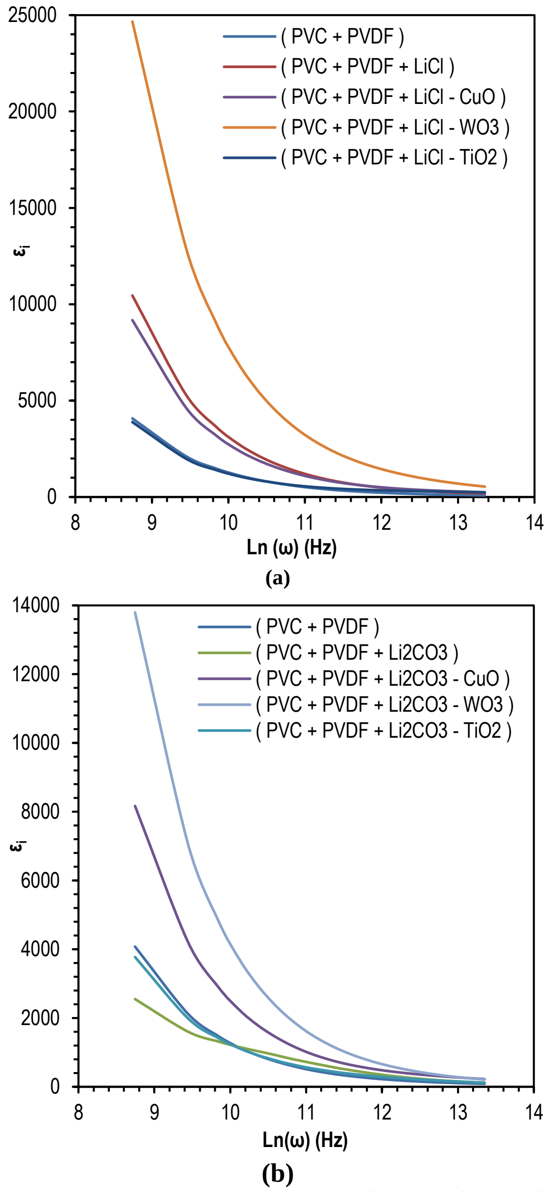


Fig. (4) Imaginary dielectric constant as function of Ln(ω) for undoped and doped PVC/PVDF/LiCl blends (a) and PVC/PVDF/Li_2CO_3 blends (b)

The DSC study of the PVC/PVDF polymer blend indicates the existence of two distinct phases within the blend, as evidenced by the observation of two glass transition temperatures at 135 and 263 ^{o}C. This phenomenon is frequently observed in polymer blends, regardless of whether they are capable of mixing or not. The doped blends exhibit a solitary glass transition temperature ranging from 50 to 300 ^{o}C, as depicted in Fig. (5), so confirming their compatibility. The influence of the fillers on the glass transition temperature (T_g) can be elucidated by the enthalpic interaction between the polymer and the nanoparticles. The addition of metal oxides decreases the T_g value. The PVC/PVDF/LiCl/CuO mix exhibited a temperature decrease from 135 to 125.09 ^{o}C, while the PVC/PVDF/LiCl/TiO_2 blend showed a temperature increase to 128.23 ^{o}C. The presence of WO_3NPs in the PVC/PVDF/LiCl/WO_3 blend decreases the T_g value to 121.74 °C. As the temperature decreases, the polymer mix undergoes an increase in flexibility and a transition to an amorphous state. The enhanced flexibility enables the transportation of ions within the polymers. As a result, the ionic conductivity is enhanced at lower glass transition temperatures.

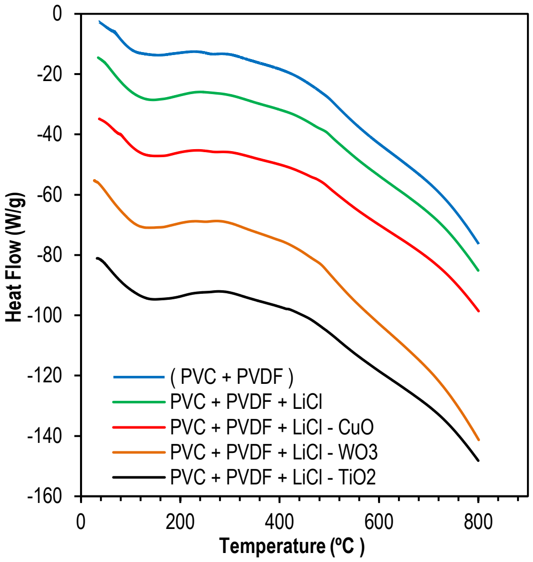


Fig. (5) DSC curves of PVC /PVDF/LiCl blends undoped and doped with metal oxides

4. Conclusion

Electrolyte films composed of PVC/PVDF/Li_2CO_3, LiCl mixes were fabricated, both with and without various metal oxide nanoparticles. The highest conductivity was associated with the lowest glass transition temperature. The values of ε_r and ε_i were influenced by the lithium salts and doping. The XRD analysis verified the presence of a semi-crystalline structure, which was reduced by the addition of lithium salts and metal oxide doping.

References

[1] Y. Lu, Q. Zhang, J. Chen, "Recent progress on lithium-ion batteries with high electrochemical performance". Sci. China Chem., 62 (2019) 533–548.

[2] R. Usiskin, J. Maier, "Interfacial effects in lithium and sodium batteries", Adv Energy Mater, 11 (2021), 2001455.

[3] S. Xin, Y. You, S. Wang, H. Gao, Y. Yin, "Solid-State Lithium Metal Batteries Promoted by Nanotechnology: Progress and Prospects", ACS Energy Lett., 2 (2017) 1385-1394.

[4] Sh. Khandare, DR. Chaudhary, B. Jha, "Bioremediation of polyvinyl chloride (PVC) films by marine bacteria", Mar Pollut Bull, 169 (2021) 112566.

[5] L. Gaabour, K. Hamam, "The change of structural, optical and thermal properties of a PVDF/PVC blend containing ZnO nanoparticles", SILICON, 10(4) (2018) 1403–1409.

[6] A.A.R. Mahmood, O.A. Hammadi and K.R. Ibraheem, "Some Physical Properties of Metal-Hydroxyquinoline Complexes in Different Solvents", *Iraqi J. Appl. Phys.*, 17(1) (2021) 9-16.

[7] A. Arya, AL. Sharma, "Polymer electrolytes for lithium ion batteries: a critical study", Ionics. 23 (2017) 497-540.

[8] A.A. Mahmood, O.A. Hammadi, K.R. Ibraheem, "Preparation and Photoluminescence Spectra of Organometallic Complexes Containing Nanoparticles as Random Gain Media", *Indonesian J. Chem.*, 22(1) (2022) 205-211.

[9] C. Smyth, **"Dielectric Behavior and Structure"**, McGraw Hill (1956), 53, 441.

[10] P. Dhatarwal, RJ. Sengwa, "Dielectric polarization and relaxation processes of the lithium-ion conducting PEO/PVDF blend matrix-based electrolytes: effect of TiO2 nanofiller", *SN Appl Sci*, 2 (2020) 833.

[11] S. B. Aziz, Z.H.Z. Abidin, A.K. Arof, "Effect of silver nanoparticles on the DC conductivity in chitosan-silver triflate polymer electrolyte", *Phys. B Condens. Matter*, 405 (21) (2010) 4429–4433.

[12] I. Hodge, "Effects of annealing and prior history on enthalpy relaxation in glassy polymers. 4. Comparison of five polymers", *Macromolecules*, 16 (1983) 898–902.

[13] M. Pollak, T. H. Geballe, "Low-Frequency Conductivity Due to Hopping Processes in Silicon", *Phys. Rev.*, 122 (1961) 1742.

[14] Y.M. Abbas, A.A. Hasan, "Dielectric and gas sensing properties of in situ electrochemically polymerized PPy-MgO-WO_3 nanocomposite films", *Iraqi J. of Science*, 62 (2021) 2915-2933.

[15] F.J. Al-Maliki, O.A. Hammadi, B.T. Chiad and E.A. Al-Oubidy, "Enhanced photocatalytic activity of Ag-doped TiO_2 nanoparticles synthesized by DC Reactive Magnetron Co-Sputtering Technique", *Opt. Quantum Electron.*, 52 (2020) 188.

[16] M.A. Hameed, S.H. Faisal, R.H. Turki, "Characterization of Multilayer Highly-Pure Metal Oxide Structures Prepared by DC Reactive Magnetron Sputtering Technique", *Iraqi J. Appl. Phys.*, 16(4) (2020) 25-30

[17] A.M. Hameed and M.A. Hameed, "Highly-Pure Nanostructured Metal Oxide Multilayer Structure Prepared by DC Reactive Magnetron Sputtering Technique", *Iraqi J. Appl. Phys.*, 18(4) (2022) 9-14.

[18] A.M. Hameed and M.A. Hameed, "Spectroscopic characteristics of highly pure metal oxide nanostructures prepared by DC reactive magnetron sputtering technique", *Emergent Materials*, 6 (2022) 627-633.

[19] A.A. Hasan, "Dielectric Study of PVC-LiF Composites Films, *Iraqi J. Sci.*, 62 (2021) 861-870.

[20] A.A. Hasan, "Synthesis and dielectric properties of MgO:ZnO composites", *Iraqi J. of Sc.*, 63(2022) 5232-5241.

[21] B.A. Hasan and D.A. Umran, "Dielectric permittivity and ac conductivity of CuInSeTe thin films", *Semicond. Sci. Technol.*, 27 (2012) (6pp) 125014.

[22] B. A. Hasan, D.A. Umran, M. A. Kadhim, "Characterization of CuInSTe/CdS Heterojunctions", The Sixth Scientific Conference "Renewable Energy and its Applications", *J. Phys.: Conf. Ser.*, 1032 (2018) 012020.

[23] B. A. Hasan, H. H. Issa, "Dielectric properties and A.C electrical conductivity analysis of $(La_2O_3)_{1-x}(ZnO)_x$", *IOP Conf. Ser.: Mater. Sci. Eng.*, 928 (2020) 072003.

[24] B.A. Hasan, H.H. Issa and A.A. Hasan, “Fabrication and Investigation of Structural, Optical and Dielectric Properties of ZnO:MnO_2 Composites”, *Iraqi J. Appl. Phys.*, 19(4A) (2023) 21-28.

[25] C. Tsonos, "Comments on frequency dependent AC conductivity in polymeric materials at low frequency regime", *Curr. Appl. Phys.*, 19(4) (2019) 491-497.