### Effect of Titanium Dioxide Nano-Fillers on the Properties of Gel-polymer Electrolytes and Power Conversion Efficiency of Dye-Sensitized Solar Cells

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#### Abstract:

TiO<sub>2</sub> nanoparticles were gradually incorporated into a gel-polymer electrolyte to optimize the nano-filler composition to develop stable and highly efficient solid-state DSSCs. For this purpose, TiO<sub>2</sub> nanoparticles (13 nm) were amalgamated (0-25%) to the polyethylene oxide-based polyiodide gel-polymer electrolyte. The Nanofiller infused electrolytes were sandwiched within six-layer photoanodes sensitized with N719 dye, and platinum electrodes to assemble DSSCs. The cell efficiency and electrolyte conductivity are highly dependent on the TiO<sub>2</sub> nanoparticle content. The electrolytic conductivity and DSSC efficiency are maximum at the optimal nano-filler percentage of 17.50%. Nanofiller-free control cell has an efficiency of 5.70%, while the optimally Nanofiller-infused DSSC shows the highest efficiency of 7.30%, yielding a 28.1% efficiency improvement. This boost in efficiency resulted in enhanced conductivity, suppression of charge recombination due to the addition of smaller-sized nanoparticles, and the utilization of an appropriate photoanode. This study uncovers valuable insights into developing more efficient DSSCs using nano-additives.

Keywords: Dye-sensitized solar cells, gel-polymer electrolytes, ionic conductivity, nano-fillers, titanium dioxide nanoparticles.

#### 01. Introduction:

In recent years, solar cells have been a focal point in energy research due to their prospected potential as a sustainable, renewable and low-maintenance energy source. Compared to most renewable energy technologies, photovoltaic technology stands out as a direct conversion method of solar energy to electrical energy. The frontrunner among photovoltaic technologies is the silicon solar cells, with efficiency being above 20% [1]. However, high production costs and complicated fabrication procedures are the main drawbacks of silicon-based solar cells [2].DSSCs have attractive characteristics such as less complicated fabrication, high environmental compatibility and sustainability, low production cost, and high efficiency under low light conditions [3,4,5]. After the successful development, of nanocrystalline TiO<sub>2</sub> thin films based DSSCs by Grätzel and O'Regan [6], numerous efforts have been made to improve the photovoltaic performance of DSSCs. So far more than 29,000 research publications have been published on DSSCs (Table 1). In general, DSSCs are composed of nanocrystalline TiO<sub>2</sub> photoanode to harvest the light energy, electrolyte containing redox couple for the regeneration of the dye and electrolyte by itself during the operation and, Pt counter electrode to collect the electrons from the external circuit [7,8,9]. Among the components of the DSSCs, the electrolyte plays a major role in improving their efficiency and operational stability [9,10]. Fig.1 shows the basic operational chemistry and charge transport in dye or quantum dot-sensitized solar cells, in 8 steps. Among the components of the DSSCs, electrolytes play a significant role in improving their efficiency and operational stability [9].

Component	Materials	6	
Photo-anode substrate	Transparent Conducting Oxide		
Photo-anode Semiconductor	TiO <sub>2</sub> (nano-porous)	2e <sup>-</sup> Conduction Band 3	
Photo- sensitizer	Dye/ Quantum dots	$2D^* \rightarrow 2D^+ + 2e^- (Oxidation) $ $\uparrow \\ 2D + 2D^* \rightarrow 2D^* LUMO \rightarrow [D^+ + e^- \rightarrow D] $	2 <b>e</b> -
Redox Electrolyte	Liquid/ Gel-polymer/ Solid	(Regeneration) $3I^{-}+2D^{+} \rightarrow I_{3}^{-}+2D$ Tri- Iodide $I_{3}^{-}+2e^{-} \rightarrow 3I^{-}$ Iodide (Redox Couple)	
Counter- electrode (Cathode)	Platinum/ Graphene	2 <i>e</i> <sup>-</sup> Ø	

Fig. 1. The chemistry and charge transport of a dye or quantum dot-sensitized solar cell.

The electrolyte governs the transfer and transport of charge carriers between two electrodes and continuously regenerates both dye and electrolyte itself during the operation of DSSCs [9]. Electrolytes suitable for high-performing DSSCs should have specific physical and chemical characteristics. The electrolyte should ensure the rapid diffusion of charge carriers between two electrodes in other word high ionic conductivity of respective redox species are needed. This causes the electrolyte and dye molecules to regenerate rapidly by themselves and maintains the high interfacial contact between the photoanode and cathode. The electrolyte should be highly stable during the operation of DSSCs. The presence of volatile, degrading, and reactive components in the electrolyte devastates the long-term stability of the cells [11]. It should also be chemically compatible with the other components (electrolyte species should not corrode electrodes) in the cells while having low cost, non-flammability and low toxicity. In particular, the liquid electrolyte-based cells should be properly sealed to prevent possible leakages and component evaporation [9,12,13]. According to the latest reports, the maximum photoconversion efficiency of DSSCs has reached 15.0% however such high-performing cells contain problematic liquid electrolytes [14, 15].

Researchers have attempted to develop DSSC by replacing liquid electrolytes with gel or solid polymer electrolytes since they offer several advantages such as high stability, ease of sealing advanced flexibility of structure design [16,17].Gel or solid polymer electrolytes provide higher stability by limiting leakage and evaporation of components in electrolytes [18,19].Solid or gel electrolytes are less flammable, safer to handle, the less prone to accidents. The use of solid or gel electrolytes can simplify the sealing process of the DSSC, making it more cost-effective and potable. Using Solid/gel polymer electrolytes flexible, flexible and lightweight DSSC devices development can be developed.

Table 1 gives an overview of the research trends in the field of dye-sensitized solar cells and the use of polymer electrolytes over the past few decades based on the Scopus database (as of 29<sup>th</sup> April 2024). Over 29,000 research publications containing the words 'dye', 'sensitized', 'solar', and 'cell' in their title, abstract, or keywords have been published. According to Scopus, about 1589 research articles relate to gel polymer electrolyte-based DSSCs. However, this survey reveals only as few as 49 publications related to nanofiller-added solar cells have been published from 1978 to April 2024. Out of those, only 12 are associated with TiO<sub>2</sub> nanofiller-based solar cells, which makes this study essential to the photovoltaics research community.

Table 1: The number of publications per year where titles, abstracts, or keywords containing
"dye + sensitized + solar + cells + (polymer electrolyte / composite electrolyte/ nanofillers /TiO <sub>2</sub>
nanofillers)" (Data retrieved from Scopus platform on 29th April 2024).

Keyword	Dye +	Dye +Dye + Sensitized + Solar + Cells+							
Year	Sensitized + Solar + Cells	Polymer electrolyte	Composite electrolyte	Nanofillers	TiO <sub>2</sub> nanofillers				
2024	454	18	15	3	2				
2023	1140	50	39	6	0				
2022	1273	70	47	3	0				
2021	1402	73	34	6	3				
2020	1551	82	37	1	0				
2019	1692	89	32	8	2				
2018	1847	103	47	5	0				
2017	1927	102	39	1	0				
2016	2152	109	60	2	0				
2015	2304	117	52	1	0				
2014	2772	115	69	4	1				
2013	2296	107	60	2	1				
2012	1933	81	33	0	0				
2011	1729	101	37	1	0				
2010	1285	90	30	3	1				
2009	866	58	14	1	0				
2008	649	57	13	2	2				
2007	499	40	16	0	0				
2006	429	38	12	0	0				
2005	343	31	11	0	0				
2004	241	21	5	0	0				
2003	156	14	1	0	0				
2002	137	14	5	0	0				
2001	70	8	0	0	0				
2000	59	0		0	0				
From 2000 to 1978	123	1	0	0	0				
Total	29329	1589	708	49	12				

# Nanotechnology to Develop DSSCs

Nanotechnology has been successfully applied in enhancing the overall efficiency and stability of the DSSCs via nano-modified electrolytes and photoanodes [20,21]. In particular, nanoscale additives such as nanofillers (NFs) can improve ionic conductivity in solid/gel polymer

electrolytes. Such electrolytes are named nanocomposite electrolytes and NFs in such electrolytes contribute to enhancing the ionic conductivity and other properties like mechanical strength. The application of such electrolytes enhances stability, minimizes internal resistance, and ensures an efficient charge transfer process within the solar cells. Because of the high surface area of such nanomaterials, nano-filler added electrolytes provide ample free space for ion diffusion and charge transport [22,23].Nano additives can enhance the interface between the electrolyte and the rest of the cell components (photoanode, photosensitive dye, and counter electrode), reducing the recombination losses and improving the charge collection and transportation [12]. Incorporation of nanoparticles into electrolytes would also prevent the aggregation of redox species, resulting in uniform charge distribution and showing stable performance of DSSCs. The use of smaller fillers is more advantageous since their surface area-to-volume ratio is higher. Therefore, the incorporation of smaller nanoparticles into electrolytes enhances the overall stability and longevity of the DSSCs.

#### *TiO*<sub>2</sub> nano-fillers

Nanoscale inorganic materials or nano-filles (NFs) can be added to DSSC electrolytes to optimize performance. Such NFs are derived from metal oxides, metal sulfides, and carbonaceous materials. These nanoparticles should have a smaller particle size than the pore size of the TiO<sub>2</sub> film of the electrode. As metal oxide material, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> nanoparticles are being used in preparing nanocomposite electrolytes [12,24,25]. Among these, TiO<sub>2</sub> metal oxide nanoparticles have attracted significant attention due to their unique and desirable characteristics along with the ease of synthesis. TiO<sub>2</sub> is an inexpensive, non-toxic and naturally occurring material. There are three different crystal phases of TiO<sub>2</sub>, namely, rutile, anatase, and brookite. The structure of rutile and anatase is tetragonal, whereas the structure of brookite is orthorhombic [26,27,28]. Various forms of TiO<sub>2</sub> nanoparticles, including nanotubes, nanospheres, and nanorods, are used as NFs for the development of polymer electrolytes for secondary batteries. High surface area, nano-porosity, optical transparency, chemical stability, substantial charge collection, high electron mobility, and wide band gap of  $TiO_2$  improve the charge transport between two electrodes, reducing the energy losses of electron-hole recombination and enhancing the light absorption. Because of that, TiO<sub>2</sub> nanoparticle-incorporated electrolytes are highly effective in the performance enhancement of the DSSCs.

### Research study and background

This study provides vital insight into systematically incorporating  $TiO_2$  nanoparticles into the gelpolymer electrolyte for DSSCs, with an emphasis on adjusting the nanoparticle percentage to determine the optimal concentration for maximum efficiency. By carefully regulating the  $TiO_2$ nanoparticle content, this research aims to clarify the effect of these nanoscale additives on the overall performance of DSSCs. Power conversion efficiency and stability of the DSSCs are highly dependent on the properties of the electrolyte. A stable electrolyte prevents the corrosion of the electrodes and desorption of dye molecules from the semiconductor materials and aids the longevity of the solar cells. Efficient electron transport maintains the continuous flow of charges and minimizes the recombination, ensuring optimal power output from the cell.  $TiO_2$  NFs enhanced the long-term stability, lowered the recombination losses, and improved the electron transport properties in order to satisfy the specifications for stable and efficient electrolytes for DSSCs, resulting in more effective and efficient solar energy devices. According to the literature, only a few research papers (12) have been published on DSSCs developed using  $TiO_2$  nanofiller-added gel polymer electrolyte as in Table 1, citing the Scopus database. A summary including filler size, host polymer, and reported efficiency is tabulated in Table 2. The maximum efficiency reported for a nanofiller-added gel electrolyte-based solar cell is 9.09%. This has been obtained with 21 nm filler particles and poly(acrylonitrile-co-vinyl acetate) polymer along with Acetonitrile as the solvent, which is volatile and toxic. In contrast, the presented study used 13 nm  $TiO_2$  nano-fillers integrated into a non-volatile and non-toxic PEO host polymer-based gel electrolytes.

Publicati on year	Numbers of publicati ons	nanofiller size	Type of polymer	Efficiency (%)	Reference
2024	1	21 nm	Polyethylene Oxide (PEO)	4.04	[29]
		13 nm	Poly(ethylene oxide)(PEO)	4.41	[30]
2021	3	240~250 nm	Polyethylene glycol (PEG)	6.10	[31]
		< 25 nm	Poly(ethylene oxide)(PEO)	5.02	[32]
2010	2	25–30 nm	Poly(vinylidene difluoride-co- hexafluoropropylene) (PVDFHFP)	5.93	[33]
2019	2	21 nm	Poly(acrylonitrile-co-vinyl acetate)	*9.09	[34]
			(NA, liquid electrolyte only	<sup>#</sup> 9.55	[34])
2014	1	21 nm	Polyethylene oxide (PEO)	4.12	[35]
2013	1	20 nm	Poly(ethylene oxide) (PEO)	2.87	[36]
2010	1	13 nm	Poly(epichlorohydrin)	3.90	[37]
2008	2	13 nm	Poly(vinylidene fluoride)	0.46	[38]
2008	2	22 nm	Polyethylene oxide (PEO)	7.19	[39]

Table 2: Summary of the publications related to DSSC with TiO<sub>2</sub> nanofiller based electrolytes.

# 02. Materials and methods:

### 2.1 Preparation of the photoanodes

The DSSCs under study were prepared using highly porous  $TiO_2$  multi-layer photo anodes that had been sensitized with a commercial ruthenium-based dye (N719). The multi-layer photoanodes were made by  $TiO_2$  nanoparticle coating on the substrate of fluorine-doped tin oxide glass (FTO).

During the preparation of the first layer of the photoanode, a slurry of TiO<sub>2</sub> nanoparticles with an average particle size of 13 nm (Evonik AEROXIDE® TiO<sub>2</sub> P 90) was spin-coated for 2 minutes at 2300 rpm on cleaned FTO glass substrates with sheet resistance  $10 \Omega \text{ cm}^{-2}$ . The TiO<sub>2</sub> slurry was prepared by mixing 0.5 g of TiO<sub>2</sub> with 2 ml of 0.1M HNO<sub>3</sub>, and the coated photoanodes were left to air-dry for approximately five hours and were sintered at 450 °C for 30 minutes. The same process was carried out during the preparation of the second layer. In order to prepare the third layer, 0.5 g of TiO<sub>2</sub> nanoparticles with an average particle size of 21 nm (Evonik AEROXIDE® TiO<sub>2</sub> P 25) were mixed with 2 ml of 0.1M HNO<sub>3</sub>. The resulting TiO<sub>2</sub> dispersion was spin-coated for two minutes at 1000 rpm prior to annealing at 450 °C. The same procedure was followed to coat the fourth, fifth, and sixth layers. Previously optimized procedures and composition were used to prepare these photoanodes [40,41,42,49].

Prepared multi-layer photoanodes were then sensitized by dipping in a 0.5 mM dye solution of N719 (Solaronix® SA) in ethanol for 24 hours. Prior to the assembly of DSSCs, photoanodes were removed from the dye solution and washed with ethanol to remove any particulates and dye molecules that were loosely attached to the FTO.

# 2.2 Preparation of the electrolyte.

All chemicals used for preparation were sourced from Sigma Aldrich®, having purity levels above 99%. LiI and Tetra-hexyl-ammonium iodide (Hex<sub>4</sub>NI) were vacuum-dried for 2 hours at ~50 °C prior to the use. The carefully measured compounds, ethylene carbonate (EC) and propylene carbonate (PC), 4-tert-butyl pyridine (4TBP), 1-methyl-3-propylimidazolium iodide (MPII), (Hex<sub>4</sub>NI), and LiI were combined in a closed vial in the proper order [42]. The resulting mixture was heated at 100 °C and was slowly added to Polyethylene oxide (PEO). After completely dissolving the PEO, the mixture was allowed to cool to 40 °C and, Iodine (I<sub>2</sub>) was added while stirring continuously. For the electrolyte. stoichiometric formula  $PEO(10)EC(40)PC(40)MPII(0.25)4TBP(0.85)Hex4NI(0.8)LiI(1.2)I_2(0.2)$ , as per the previously optimized procedure [42,43]. In order to prepare the TiO<sub>2</sub> nanoparticle-infused electrolyte, after adding PEO relevant amount of TiO<sub>2</sub> nanoparticles were added with an average particle size of 13 nm at 0.0 to 25.0 wt.%. Before analyzing the gel-polymer electrolyte, it was kept at room temperature for forty-eight hours. The weight and weight percentage of the constituent of each sample are tabulated in Table 3.

 Electrolyte	TiO <sub>2</sub> wt.%	TiO <sub>2</sub> / mg	PEO / mg
Sample A	0.00	0.00	50
Sample B	2.50	1.25	48.75
Sample C	5.00	2.50	47.50
Sample D	7.50	3.75	46.25
Sample E	10.00	5.00	45.00

Table 3: The percentage of TiO2 NFs, TiO2 NFs weight, and PEO weights for electrolyte samples.

Sample F	12.50	6.25	43.75
Sample G	15.00	7.50	42.50
Sample H	17.50	8.75	41.25
Sample I	20.00	10.00	40.00
Sample J	22.50	11.25	38.75
Sample K	25.00	12.50	37.50

# 2.3 Preparation of DSSCs.

The gel-polymer electrolytes were sandwiched between the photo-sensitized multi-layer anodes and the platinum (Pt) counter-electrodes to assemble DSSCs.

### 2.4 Characterization

After preparing the DSSCs, characteristic parameters of DSSCs were obtained using a PEC-LO1 solar simulator under AM1.5 (1000 W m<sup>-2</sup>) radiation conditions with the support of a potentiostat [Peccell® Technologies] device. The active cell area was 0.19 cm<sup>-2</sup>. Data for current versus voltage were obtained under continuous irradiation.

To examine the electrochemical resistance of the electrolyte series and DC polarization, a Metrohm® Autolab PGSTAT128N instrument was used within the frequency range 0.1 Hz to 1.0 MHz at different temperatures from 20 °C to 80 °C. There, the nanoparticle-incorporated gelpolymer electrolyte samples of 1 mm thickness and 9 mm diameter were sandwiched between two stainless steel electrodes.

To examine the FTIR spectra and morphology of the gel-polymer electrolyte, a Fourier transform infrared (FT-IR) spectroscopy (FT/IR-6700 Spectrometer from JASCO®) and ZEISS® AXIO Lab.A1 Polarizing Laboratory Microscope by Primotech® were used.

### 03. Results and Discussion:

### 3.1 Complex Impedance Analysis

### 3.1.1 DC conductivity

The Nyquist plots of the  $TiO_2$  NFs incorporated electrolyte series obtained at various temperatures are shown in Fig. 2(a). As an example, the Nyquist plots of the high conducting electrolyte (sample H) taken at different temperatures ranging from 20 °C to 80 °C are shown in Fig. 2(a). Every other sample (A to K) also exhibits similar curves. Table 4 displays the ionic conductivity values of the NFs incorporated electrolyte series.



**Fig. 2.** (a) Nyquist plots for electrolyte sample H (Containing  $17.5 \text{ wt.}\% \text{ TiO}_2$  nanoparticles) taken at various temperatures, (b) conductivity variation with TiO<sub>2</sub> compositions of the electrolyte samples at different temperatures, (c) conductivity Arrhenius plots of the electrolytes series, and (d) Vogel-Tammann-Fulcher (VTF) plots of the electrolyte series.

**Table 4:** Conductivity value for all electrolyte series with TiO<sub>2</sub> NFs added with various temperatures.

Temp (	perature ( <i>T</i> )	Conductivity ( $\sigma$ / mS cm <sup>-1</sup> )										
T/°C	T/K			Т	iO <sub>2</sub> NF	s added	gel-pol	ymer ele	ctrolyte	sample		
1/ C 1/K		A	В	С	D	Е	F	G	Н	Ι	J	K
20	293.15	3.34	3.70	3.92	4.31	4.27	4.60	4.58	5.18	4.60	4.47	3.93
30	303.15	3.82	4.13	4.80	5.03	4.91	5.29	5.48	6.36	5.06	5.03	4.21
40	313.15	4.72	5.05	5.42	6.02	5.87	6.31	6.49	7.18	5.85	5.65	4.57
50	323.15	5.45	5.90	6.04	6.87	6.81	7.11	7.38	8.06	6.58	6.33	5.14

60	333.15	6.08	6.49	6.85	7.73	7.62	7.84	8.14	8.95	7.24	6.98	5.78
70	343.15	6.73	7.03	7.57	8.52	8.42	8.71	9.05	9.77	7.72	7.45	6.64
80	353.15	7.37	7.41	8.36	9.11	9.01	9.17	9.73	10.43	8.15	8.10	7.27

The DC resistance values of the electrolyte were derived by using the Nyquist plots to calculate the ionic conductivity of the electrolyte series. The conductivity values for these NF-incorporated electrolyte samples usually show enhanced conductivity at high temperatures due to the mobility enhancement of ions at elevated temperatures. Those DC resistances of electrolytes obtained were used to determine the ionic conductivity of the NF-infused electrolyte series, as depicted in Fig. 2(b).

The conductivity variation of the electrolyte series upon TiO<sub>2</sub> composition at different temperatures is shown in Fig. 2(b). The ionic conductivity of nanoparticle-incorporated electrolytes enhances with the increase of TiO<sub>2</sub> nanoparticle percentage up to 17.5%. In this sample, the conductivity of 5.18 mS cm<sup>-1</sup> at 20 °C enhanced to 10.43 mS cm<sup>-1</sup> when the temperature raised to 80 °C. The increased amount (up to 17.5%) of TiO<sub>2</sub> NFs causes the separation of polymer chains in the PEO network and re-arranges them in a three-dimensional network, creating more free space. The free spaces act as additional pathways for the migration of the I<sup>-</sup>/I<sup>-</sup><sub>3</sub> ions through the electrolyte. TiO<sub>2</sub> NFs contribute to this process by inducing electrostatic interactions / Lewis acid-base interactions between O atoms of the PEO and hydroxyl group of the TiO<sub>2</sub> particles [12,12]. These Lewis acid-base type interactions stabilize TiO<sub>2</sub> NFs on the surface of the PEO and prevent the recrystallization of polymer chains. Additional TiO<sub>2</sub> NFs contribute to the improvement of the ionic conductivity of the electrolyte by changing the morphology of the polymer network. As the TiO<sub>2</sub> particle concentration in the electrolyte increases further (above 17.5%), immobilized long polymer chains and NF aggregates will be formed, decreasing the conductivity of the electrolyte above 20 °C. This effect is known as the blocking effect of nanofillers or geometrical constrictions [12,12,44,45,46].

### 3.1.2 Temperature Dependence of the Ionic Conductivity

Temperature dependence of ionic conductivity demonstrated non-Arrhenius behavior for all electrolyte samples in the series. The ionic conductivity of nanoparticle incorporated electrolyte increases with the increase of TiO<sub>2</sub> nanoparticle percentage. As shown in Fig. 2(c), the maximum conductivity is shown by the electrolyte sample H, which has 17.5 wt.% TiO<sub>2</sub>. The low-temperature (20 °C) conductivity of this electrolyte sample was 5.18 mS cm<sup>-1</sup>, and a high-temperature conductivity of 10.43 mS cm<sup>-1</sup> was shown at 80 °C. It was also observed that the conductivities of all TiO<sub>2</sub> nanocomposite electrolytes in the examined temperature range (from 20 °C to 80 °C) are closer to each other. In general, the observed conductivity value of all the investigated electrolyte samples was significant enough to fabricate high-performance nanocomposite gel-polymer electrolyte DSSCs.

Since the temperature dependence of conductivity was non-Arrhenius, the conductivity values were fitted using the Vogel-Tammann-Fulcher (VTF) model as in Eq. 1. The corresponding VTF plots are shown in Fig. 2(d), and it demonstrates the validity of VTF behavior in temperature dependence conductivity [46]. In this model fitting, the glass transition temperature  $(T_0)$  of the

samples was considered as -100 °C, and the appropriate selection is reflected by the better fitting shown in Fig. 2(d). There,  $\ln(\sigma T^{1/2})$  was plotted against  $1000/(T-T_0)$ , and the behavior of the electrolytes at various temperatures was examined using individual VTF plots. The fitted data confirms a linear trend. Furthermore, the pseudo activation energy and pre-exponential factors were calculated by fitting the data to the VTF equation and included in Table 5. The free exponential factor, which is a measure of free ion concentration, fluctuates between 2.6 and 3.9 S cm<sup>-1</sup> K<sup>1/2</sup>. This variation can be attributed to the synergistic effects of the ion dilution effect and ion association/dissociation, driven by the escalating mass fraction of TiO<sub>2</sub>. The observed decreasing  $E_a$  (drop in the activation energy) with the increasing TiO<sub>2</sub> content underscores the nano-filler's role in enhancing conductivity. The increase in conductivity of the electrolyte samples upon temperature increase can be attributed to the enhancement of mobility of ions at elevated temperatures resulting in decreased activation energy [47,48].

$$\sigma(T) = AT^{-\frac{1}{2}} \exp\left[\frac{-Ea}{K_b(T-T_0)}\right]$$
(1)

**Table 5:** The pre-exponential factor, A and activation energy,  $E_a$  for all electrolyte series with varying TiO<sub>2</sub> NFs percentages from 0.0% to 25.0%.

Sample	$A / S \text{ cm}^{-1} \text{ K}^{1/2}$	$E_{\rm a}$ / eV
A	3.9	2.6
В	3.6	2.5
С	3.6	2.5
D	3.9	2.5
Е	3.9	2.5
F	3.6	2.4
G	3.8	2.4
Н	3.6	2.3
Ι	2.6	2.0
J	2.6	2.0
K	2.7	2.1

#### 3.1.3 Complex AC Conductivity

Generally, the complex conductivity of an electrolyte depends on the different kinds of polarization, such as dipole polarization, ionic polarization, electronic polarization as well as the polarization of the electrodes [49]. Furthermore, the ionic conduction and dielectric behavior of the electrolytes get modified by the dynamics of charge species along with dipole and dielectric relaxation [46, 50]. Because of this complexity, the electrolyte examined in this study is expected to experience a variety of polarization mechanisms. Because of that, the real part ( $\sigma$ ) and

imaginary part ( $\sigma''$ ) of the AC conductivity of electrolyte series with NFs are studied as a function of frequency at different temperatures from 20 °C to 80 °C.

The variation of the frequency-dependent real part of the AC conductivity of sample H (with 17.5 wt.%  $TiO_2$  NFs) is shown in Fig. 3(a) for several temperatures. All other samples (A to K) exhibited a similar trend. The real part of the AC conductivity increases with the increase in frequency due to the enhanced frequency-dependent polarization dynamics.

The AC conductivity reaches the DC limit at high frequencies, and these high-frequency values are similar to the DC conductivity values obtained via Nyquist plots as in Fig. 2(a). All the conductivity curves for the electrolyte series tend to plateau at high frequencies as well as low frequencies. AC conductivity for the samples onsets a high-frequency plateau at  $10^5$  Hz as tabulated in Table 6. Also, due to the mobility enhancement of ions at elevated temperatures, these high-frequency plateau values increase with temperature for all electrolyte samples in the series.

Temp	erature		A C conclustivity of $105 \text{ Hz} (-100 \text{ cm}^2)$									
(	(T)		AC conductivity at $10^{\circ}$ HZ ( $\sigma$ / mS cm <sup>-1</sup> )									
T/°C	T/V			Т	iO <sub>2</sub> NF	's added	gel-pol	ymer ele	ctrolyte	sample		
<i>I/</i> C	<i>1</i> /K	A	В	С	D	Е	F	G	Н	Ι	J	K
20	293.15	1.18	1.29	1.37	1.50	1.49	1.61	1.61	1.81	1.61	1.56	1.38
30	303.15	1.34	1.45	1.68	1.76	1.72	1.92	1.92	2.23	1.77	1.77	1.47
40	313.15	1.65	1.77	1.89	2.11	2.05	2.27	2.27	2.51	2.05	1.98	1.59
50	323.15	1.91	2.06	2.11	2.41	2.38	2.58	2.58	3.12	2.31	2.21	1.79
60	333.15	2.13	2.26	2.39	2.69	2.66	2.84	2.84	3.17	2.54	2.44	2.02
70	343.15	2.35	2.45	2.64	2.96	2.93	3.15	3.15	3.41	2.70	2.60	2.32
80	353.15	2.57	2.59	2.91	3.17	3.13	3.39	3.39	3.63	2.85	2.82	2.55

**Table 6:** AC conductivity for all electrolyte samples from A to K infused with  $TiO_2$  nano-fillers at  $10^5$  Hz for various temperatures.

As seen by Fig. 3(a) and its inset for representative sample H, the real part of the AC conductivity ( $\sigma'$ ) exponentially drops while approaching low frequencies (100 Hz to 1 Hz). All other samples (A to K) exhibit similar behavior as well. This exponential drop can be traced to the relaxation of electrode polarization. At low frequencies, there are fewer mobile ions in the bulk due to the increased charge build-up at the electrode-electrolyte interface. The low-frequency conductivity is decreased due to this charge carrier deficit [51]. In order to understand the polarization effects governed by ionic motion in the bulk, the low-frequency part of the  $\sigma'$  is fitted to Eq. 2 [52].

$$\sigma'_{(\omega)} = A\omega^n \tag{2}$$



Where  $\omega$  is the angular frequency of the applied AC signal, and *n* is a factor that depends on the polarization.

Fig. 3. Frequency dependence of (a) the real part of the AC conductivity ( $\sigma'$ ) (Inset shows the low frequencies values), (b) the imaginary part of the AC conductivity ( $\sigma''$ ), (c) the real part of the dielectric constant ( $\varepsilon'$ ) and (d) the imaginary part of the dielectric constant ( $\varepsilon''$ ) of the electrolyte sample H (that contains 17.5 wt.% TiO<sub>2</sub> NFs) at various temperatures.

The imaginary part of the AC conductivity ( $\sigma''$ ) for sample H is also frequency dependent, as depicted in Fig. 3(b). All the samples (A to K) show a similar trend, with the peaks growing upward with increasing temperature. The relaxation of interfacial charge transport contributes to the peak value of the  $\sigma''$  AC conductivity. Typically, the imaginary part,  $\sigma''$ , is due to the capacitive effects of the cell prepared by sandwiching an electrolyte between two stainless steel blocking electrodes.

### 3.1.4 Dielectric Constant (ε)

The polarization between the interfaces and the bulk affects the dielectric characteristics of the electrolyte system. Dielectric polarization of the electrolyte plays a significant role in the relative mobility of the positive and negative charges within the assembled cells. The dielectric response of an electrolyte can be characterized by the relative dielectric constant as a complex quantity made up of real and imaginary parts. There, the real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of the dielectric constant

represent the quantity of energy stored in an electrolyte material as polarization and energy loss as a function of the applied electric field [53]. The real and imaginary parts of the dielectric constant can be obtained using Eq. 3 and 4 [50].

$$\varepsilon' = -\frac{Z''}{\omega C_0 (Z''^2 + Z'^2)}$$

(3)

$$\varepsilon'' = \frac{Z'}{\omega . C_0 (Z''^2 + Z'^2)}$$

(4)

Where the real part of the impedance, the imaginary part of the impedance, the angular frequency, and the geometrical capacitance are represented by the symbols  $Z', Z'', \omega$ , and  $C_0$ , respectively.

The variations of the real part of the dielectric constant ( $\varepsilon'$ ) with frequency for sample H, plotted for different temperatures from 20 °C to 80 °C, are shown in Fig. 3(c). All other samples (A to K) exhibit similar behavior. The curve shows a decrease of the dielectric constant with the increase in frequency at constant temperature. This behavior can be attributed to the fact that relaxation (orientation and interfacial) and deformational polarization (electronic and ionic) contribute to the dielectric constant value at low frequencies. The orientation and interfacial polarization are significantly dominant at low frequencies [54].

The frequency dependence of the imaginary part ( $\varepsilon''$ ) of the dielectric constant for sample H is captured in Fig. 3(d) for a range of temperatures between 20 °C and 80 °C. The curves demonstrate a decrease of the  $\varepsilon''$  with the increase in the frequency at constant temperature. Furthermore,  $\varepsilon''$  increases due to the increase in the temperature at a constant frequency. At higher temperatures, dipoles can quickly orient themselves with the field, leading to an increase in the dielectric constant [50,55]. Also, the imaginary part of the dielectric constant contributes to the DC conductivity at low temperatures [50].

#### 3.2 Polarizing Microscopy Analysis:

PEO is abundantly used in preparing gel-polymer electrolytes due to its favorable physicochemical properties. The single helical structure of PEO results in rapid ionic conduction, but PEO is semicrystalline at room temperature [56]. The crystallization of the PEO can be controlled by adding  $TiO_2$  nanoparticles, which increases the ionic conductivity of the electrolyte.  $TiO_2$  nanoparticles change the PEO polymer matrix and increase the amorphousity of the electrolyte. This creates free spaces, which improves ionic transport [57].

The polarization microscopic images of the electrolyte series obtained by varying  $TiO_2$  nano-filler percentage from 0% to 25% are shown in Fig. 4(a) to (k). The polarization microscope image of pure PEO polymer is shown in Fig. 4 (l) for comparison. The spherulites formed by lamella

structures visible in pure PEO samples are not visible in the electrolyte samples [58, 59]. The microscopic images show the improvement of the amorphousity of the polymer matrix with increasing NF infusion, as well as a uniform distribution of the AFs within the matrix.



- **Fig. 4.** Polarizing micrographs of (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F, (g) sample G, (h) sample H, (i) sample I, (j) sample J, (k) sample K, and (l) Pure PEO sample under the magnification ×10×40.
- 3.3 DC Polarization Analysis:



**Fig. 5.** DC polarization curves of all electrolyte series with varying  $TiO_2$  percentages from 0% to 25%.

For DC polarization measurements, gel-polymer electrolytes were sandwiched between the two stainless steel blocking electrodes with a 0.64 cm<sup>2</sup> hole area with 1 mm thickness. These stainless-steel blocking electrodes are suitable for determining the transference number of electrons and ions because only electrons can be passed through these electrodes. The ratio of the measured polarization current to maximum polarization current versus time for the electrolyte series is shown in Fig. 5. The measurements were taken continuously for 30 minutes. The transference number of ions and electrons was obtained from the graph using Eq. 5 and 6.

$$T_{ion} = \frac{I_{ion}}{I/I_{max}} \tag{5}$$

$$T_e = 1 - I_{ion} \tag{6}$$

Where the ionic transference number, electronic transference number, ionic current, electronic current, current of polarization, and maximum current of polarization are represented by the symbols  $T_{ion}$ ,  $T_e$ ,  $I_{ion}$ ,  $I_e$ , I, and  $I_{max}$ , respectively.

When the migration of ions reaches equilibrium, the current approaches the steady state. Within the gel-polymer electrolyte, ions act as dominant charge carriers. Because of that, a drastic drop in the current can be seen in the graphs before reaching the steady-state current. If, instead, the electrons were the dominant charge carrier, this drastic current drop of the current would not be visible. It is possible to conclude that the gel-polymer electrolytes under study consist of ionic charge carriers by using the saturated levels of polarization current [60, 61]. Based on the graph, all electrolyte samples report ionic transference numbers between 0.96 and 0.99. Since ions have a significant contribution to the conductivity of electrons, it has been further confirmed that all electrolyte samples are good ionic conductors.

### 3.4 FTIR Analysis:



**Fig. 6.** FTIR spectra recorded from 250 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> for the electrolyte series with TiO<sub>2</sub> percentages varying from 0% to 25%.

A set of FTIR spectra for the electrolyte series is shown in Fig. 6, with the wavenumber scanned from 500 cm<sup>-1</sup> to 3000 cm<sup>-1</sup>. It indicates the vibration frequencies of molecular bonds associated with EC and PC organic solvents in each electrolyte sample. The FTIR spectra demonstrate the inplane ring stretching, asymmetric ring stretching, and C – O stretching frequencies at 714.50 cm<sup>-1</sup>, 1069.34 cm<sup>-1</sup>, and 1770.33 cm<sup>-1</sup>, respectively. The vibration frequencies correspond to the out-of-plane ring bending, C – H wagging, and C – H rocking appear at 772.35 cm<sup>-1</sup>, 1158.04 cm<sup>-1</sup>, and 1388.49 cm<sup>-1</sup>, respectively [60, 62]. Peaks corresponding to additional vibration frequencies

are not visible in this FTIR spectra. The data further confirms that the electrolyte is suitable for DSSCs and that there are not any undesired chemical components or byproducts within the electrolytes.

#### 3.5 Characterization of DSSCs

The current density variation with the cell potential of DSSCs assembled using the above-analyzed series of electrolytes having various mass percentages of  $TiO_2$  nanoparticles are shown in Fig. 7(a). Such curves were used to calculate the open circuit voltage (*Voc*), short circuit current density (*Jsc*), power conversion efficiency (PCE), and fill factor (*ff*) of the cells. The fill factor and PCE of the cells were determined using Eq. 7 and 8.

$$ff = \frac{(V_{opt} \times J_{opt})}{(V_{oc} \times J_{sc})}$$
(7)

$$PCE = \frac{(V_{opt} \times J_{opt} \times ff)}{Total \, Incident \, Power} \times 100\%$$
(8)



**Fig. 7.** The variation of (a) current density and (b) power density against cell potential for the DSSCs prepared with the electrolyte series.

In general, the charge transport process of a DSSC depends highly on the conductivity of its electrolyte. The resistance of the electrolyte is a major contribution to the overall resistance of the DSSC devices, and it depends on the electrolyte's conductivity. The short circuit current density and the photocurrent of a DSSC are controlled by the conductivity of the electrolyte.

In this study, the highest photo conversion efficiency was delivered by the DSSCs with the electrolyte (Sample H) containing 17.50 wt.% TiO<sub>2</sub> NFs. There, the *J*sc and *V*oc values were 13.30 mA cm<sup>-2</sup> and 0.78 V, respectively, for this DSSC. The variations of power density with the cell potential of the DSSCs for the electrolyte series are shown in Fig. 7(b).



**Fig. 8.** Variation of the energy conversion efficiency in DSSCs assembled with TiO<sub>2</sub> nanofiller-infused electrolytes.

The variation of energy conversion efficiencies in the DSSCs assembled using the electrolyte series is shown in Fig. 8. Each cell measured in this study shows efficiencies above 5%. The prototype DSSC assembled with the highest conducting electrolyte (Sample H; containing nano- $TiO_2$  17.50 wt.%) yields the highest efficiency of 7.30%. Consequently, there is a 28.1% power enhancement compared to the efficiency of the reference DSSC assembled with a standard gelpolymer electrolyte (5.70%). The gel-polymer electrolytes under investigation do not contain any volatile solvents like ethanol, acetone, or methanol. In this study, the fabricated DSSCs are stable and environmentally friendly, with a high photo conversion efficiency of up to 7.30%. Compared to values given in Table 2 the present study reports the highest efficiency for a PEO-based  $TiO_2$  nanofiller-integrated DSSCs.

#### 4.0 Conclusions

The presented study is on the gel-polymer electrolyte modified by infusing nano-fillers (NFs), which is suitable for fabricating environmentally friendly and stable dye-sensitized solar cell

DSSCs with high energy conversion efficiency. NFs used here are TiO<sub>2</sub> nanoparticles. The ionic conductivity of the electrolytes initially increases with an increase in TiO<sub>2</sub> content up to 17.5% TiO<sub>2</sub> and then decreases with any further increase in TiO<sub>2</sub> percentage. The optimum TiO<sub>2</sub> content in the electrolyte is 17.5%; for both conductivity and DSSC performance. Also, the temperature-dependent ionic conductivity of the electrolyte series showed non-Arrhenius behavior. The maximum conductivity values reported for all the temperatures from 20 °C to 80 °C were given by the electrolyte sample infused with 17.5 wt.% of TiO<sub>2</sub> NFs (sample H). Those conductivity values are 5.18, 6.36, 7.18, 8.06, 8.95, 9.77, and 10.43 mS cm<sup>-1</sup> at 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C respectively. The frequency-dependent electrical and dielectric characteristics of electrolytes were analyzed in terms of real and imaginary parts of the AC conductivity. The real part of the AC conductivity exponentially decreases with the decrease as well as with the decrease in temperature; the imaginary parts of the AC conductivity peak between 1 kHz and 10 kHz.

The development of the amorphousity of the polymer network with the increase in NF amount is evident from the polarization micrographs, which result in improving the conductivity of the electrolyte. DC polarization analysis reveals that the ionic transference number of all electrolyte samples is greater than 0.96. This signifies a higher ionic contribution to the conductivity, inferring that the nano-infused electrolytes under study can be considered efficient electrolytes.

In order to further characterize the performance of the nano-modified electrolytes, prototype DSSCs were assembled using commercial N719 sensitizer dye, TiO<sub>2</sub>-based photoanodes, and standard platinum counter electrodes. Every cell showed efficiency above 5%. The DSSCs assembled with the electrolyte sample containing the optimal amount (17.5 wt.%) of TiO<sub>2</sub> NFs yielded a maximum efficiency of 7.30%, resulting in a 28.1% power enhancement compared to DSSCs assembled with standard gel-polymer electrolyte. Therefore, this study provides valuable insights into the potential role of nano-filler-infused gel-polymer electrolytes in developing high-performance DSSCs that are non-toxic, stable, and efficient.

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