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Electrical conductivity of titanium dioxide ethylene glycol-based nanofluids: Impact of nanoparticles phase and concentration

Jacek Fal^{a,*}, Jolanta Sobczak^b, Ryszard Stagraczyński^a, Patrice Estellé^c, Gawel Żyła^a

^a*Department of Physics and Medical Engineering, Rzeszow University of Technology, Rzeszow, Poland*

^b*Doctoral School of Engineering and Technical Sciences at the Rzeszow University of Technology, Rzeszow, Poland*

^c*Laboratoire de Génie Civil et Génie Mécanique, LGCGM, Université Rennes, 35000 Rennes, France*

Abstract

Nanofluids containing titanium oxide nanoparticles are one of the most often investigated by researchers and their properties such as viscosity or thermal conductivity were largely reported. On the other hand, electrical conductivity of this type of nanofluids are often omitted. Therefore, this paper reports experimental data on the electrical conductivity of ethylene glycol based nanofluids with three types of titanium dioxide nanoparticles dispersed in it. Samples of all nanofluids were prepared in mass fraction between 0.01 and 0.20, and for this purpose well known two-step method was used. The electrical conductivity was measured in temperature range from 10 to 45 °C. The results show effect of TiO₂ nanoparticles content on electrical conductivity of ethylene glycol as well as the influence of nanoparticles phase. The highest enhancement has been noted for anatase at lowest tested temperature. Finally the experimental data were compared to available models and a new theoretical correlations was proposed.

Keywords: nanofluid, titanium dioxide, anatase, rutile, electrical conductivity

* Corresponding author

Email address: jacekfal@prz.edu.pl (Jacek Fal)

1. Introduction

The intensive growth in nanofluids research observed for over twenty years was initiated by Choi et al. [1]. Since this time, many papers concerning nanofluids have been published and their number increase from year to year. Carbon-based material as new type of nanomaterials including multiwalled carbon nanotubes [2, 3], nanofibers [4], graphene [2, 5] or fullerenes [6, 7, 8] are largely considered. Also, more regular and traditional materials, such as metals [9] or oxides [10], are used in the preparation of nanofluids and show interesting thermophysical properties. One of the most often used nanoparticles are oxides and among them is titanium dioxide (TiO_2) which is cheap and generally well characterized [11, 12, 13]. TiO_2 nanoparticles are well known as semi-conductors for photocatalytic applications in a wide range of fields, including energy and environment [14, 15]. They can be found under three crystalline forms, namely anatase, rutile and in a less extend brookite. Stable rutile comes from the transformation of metastable anatase (or brookite) at high temperature and can be obtained under various processes and methods as reviewed in [15]. Anatase and rutile have a tetragonal structure sharing four and two edges, respectively. The reader is referred to the study by Hanaor and Sorrel [15] for a comprehensive differentiation between anatase and rutile species, and their ratio following the synthesis conditions followed. Like dry TiO_2 nanoparticles, nanofluids containing this type of nanoparticles are also widely investigated. The percentage distribution of studied properties of titanium oxide based nanofluids, presented in Fig. 1, shows that the researchers mainly focused on the thermal conductivity and viscosity of those types of nanofluids. Rheological behavior of ethylene glycol-based nanofluids containing TiO_2 nanoparticles was examined by many reserchers [16, 17, 18, 19]. It was presented that nanofluids containing high fraction of particles exhibit non-Newtonian nature [16, 18], while a low fraction generally induces a Newtonian one [17]. Thermal conductivity of TiO_2 -EG nanofluids was also well studied, as shown in Refs. [17, 19, 20, 21]. More information about the thermophysical properties of various nanofluids could be found in the state-of-the-art review paper by Qiu et al. [22].

Figure 1: Percentage distribution of studied properties of titanium oxide based nanofluids, based on Web of Science, 2021-09-07.

As illustrated by Figure 1, the Web of Science database evidence that only few papers considering nanofluids containing titanium dioxide nanoparticles in various base fluids and their electrical properties were published (data collected at 07-09-2021). A short summary of the main studies in this field is presented in Table 1. The most often used base fluid for titanium dioxide nanofluids is water (W).

Awin et al. [13] studied the electrical conductivity (EC) of nanofluids based on titanium dioxide dispersed in water with volume concentration of 0.0015 – 0.005%. The electrical conductivity of nanofluids was obtained from two different methods. Firstly, the authors evaluated the electrical conductivity based on the refractive index and the absorbance. Next, both results were compared and good agreement between them was confirmed. The results confirm increase in electrical conductivity with increasing of TiO_2 nanoparticles in base fluid. For the lowest (0.0015%) and the highest (0.005%) tested volume concentration the electrical conductivity was approximately $2.3 \mu\text{S}/\text{cm}$ and $2.75 \mu\text{S}/\text{cm}$ at 25°C respectively. Titanium dioxide-water nanofluids were also studied by Angayarkanni et al. [23], but data concerning electrical conductivity are presented in a limited way. Only one concentration (4% in vol.) and temperature (25°C) were tested, but a large enhancement in EC of about 8876% was reported. Chereches and Minea [24] also studied titanium dioxide water-based nanofluids in volume concentration range 1-3 %. They reported an increase in electrical conductivity from $25.77 \mu\text{S}/\text{cm}$ for pure water to approximately 800 and $1500 \mu\text{S}/\text{cm}$ for 1 and 3 vol% respectively. Moreover, the favourable effect of temperature on the electrical conductivity of titanium dioxide water-base nanofluids was also highlighted. Electrical conductivity of titanium dioxide water nanofluid was also studied by Sikdar et al. [25]. The nanoparticles used to prepare nanofluids with volume concentration range of 0.5% to 3.0% were a mixture of two TiO_2 phases, anatase 76% and rutile 24% respectively. Investigations were conducted for four temperatures ($24, 34, 40, 45^\circ\text{C}$) and show 25-fold and 80-fold increase in electrical conductivity for 0.5 and 3.0 vol% respectively. For those date the simple correlation with two factor were also introduced.

Table 1: Summary of electrical properties of TiO_2 nanofluids with various base fluids.

Another group of titanium dioxide nanofluids are those based on the mixture of water and

ethylene glycol (W/EG). As a part of preliminary studies, dispersion of TiO_2 nanoparticles in a mixture of water and ethylene glycol was investigated by Islam et al. [26] in the context of applications in Proton Exchange Membrane Fuel Cell (PEMFC). They showed 890% enhancement in electrical conductivity for water/ethylene glycol nanofluids containing 0.5 vol% TiO_2 nanoparticles. Islam et al. [27] investigated of the electrical properties of nanofluids prepared by two-step method in volume concentrations of 0.05 to 0.5 %. The base fluid was prepared as a mixture of ethylene glycol and water in ration 1:1 with dispersed TiO_2 nanoparticles. They observed approximately 90% and 50% increase in electrical conductivity for increase in temperature from 20 to 70 °C for 0.05 and 0.5 vol% respectively. Islam et al. [28] again presented research on the electrical conductivity titanium dioxide water/ethylene glycol nanofluids with volume concentration between 0.05 and 0.5%. They proposed a new correlation for predicting values of electrical conductivity in the studied range of nanoparticles content and temperatures.

Kumara et al. [29] studied the impact of titanium dioxide nanoparticles on electrical properties of pure ethylene glycol (EG) and their mixtures with two type of surfactants. Using two step method they prepared samples with mass concentration ranging from 0.05 to 1.0 %. The studies conducted at temperature range from 30 to 90 °C show that the electrical conductivity is enhanced by increase in load of TiO_2 nanoparticles. Also, addition of both surfactants causes slight increase in electrical conductivity, especially in lower tested temperatures; for higher temperatures this effect was weaker. The maximum value of electrical conductivity was obtained for the highest tested mass concentration (1.0 wt%) of TiO_2 nanoparticles supported by SDS surfactant.

The effect of TiO_2 nanoparticles on EC of oil (O) was studied by Cieśliński et al. [30]. They presented results for nanofluids based on thermal oil with dispersed of TiO_2 nanoparticles 47 nm in average diameter and revealed a decrease in electrical conductivity with increasing temperature.

In the most of the published works, the authors highlighted the incompatibility of classical models of electrical conductivity and introduced their own empirical correlations to describe the dependency of electrical properties on the concentration of nanoparticles and temperature, which are mostly suitable only for one specific nanofluid. Therefore, it is important to

provide new experimental data to contribute to the development of better models describing the electrical properties of nanofluids. The availability of more experimental data on the electrical conductivity of various nanofluids can help in the work, both theoretical and numerical, on the preparation of a uniform model of the electric conductivity of nanofluids that could be used in numerical simulations and theoretical analysis as example. In this paper, the electrical conductivity of ethylene glycol based TiO_2 nanofluids, considering three different types of nanoparticles, with range of mass fraction (0.01–0.20) was presented. The dependence of electrical conductivity on mass fraction and temperature was investigated.

2. Materials and Methods

2.1. Materials

In this study, three different types of TiO_2 nanoparticles were used. All of them are commercially available on the market and were purchased from PlasmaChem GmbH. According to the manufacturer data, one of them should be in anatase phase (labelled as TiO_2 A), the second in rutile phase (labelled as TiO_2 M1) and the third is a mixture of both anatase and rutile phases (labelled as TiO_2 M2) with average diameter 4-8 nm, 2 nm and 21 nm respectively. To confirm properties declared by the manufacturer, a series of measurements were performed including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Brunauer, Emmett and Teller (BET) characterizations as explained in section 3.1. Ethylene glycol (EG) manufactured by Fisher Chemical (Loughborough, UK, purity over 99%) was used as the base fluid.

2.2. Nanofluid preparation

For the purpose of this study three types of titanium (IV) oxide (TiO_2) nanoparticles were used to produce nanofluids with various mass concentration from 1 to 5% with 1% step. In addition, higher concentrations 10, 15, 20% were also considered.

Nanofluid samples were obtained by the two-step method. Firstly, the right amount of nanopowder has been weighed using an analytic balance (Pioneer Semi-Micro PX225DM, OHAUS Corporation, Parsippany, NJ, USA, an accuracy of 0.01 mg). Next step was adding the

base fluid and mechanical stirring for 30 min using Genius 3 Vortex (IKA, Staufen, Germany). Later in order to break potentially remaining agglomerates in nanofluids the ultrasonic bath (Emmi 60 HC EMAG, Moerfelden-Walldorf, Germany) was employed for 200 minutes. The last stage included a high-energy ultrasounds procedure with a probe (Sonics Vibracell VCX130, Sonics & Materials Inc., Newtown, USA) for 5 min in order to ensure a good homogeneity of the sample. No surfactant were used during the preparation and the samples were immediately investigated after preparation. Based on the visual observation nanofluids were stable at least 6 hours after preparation, which was enough to perform all measurements. After this time the sedimentation occurs. The relation between the volume and the mass fraction of mentioned nanofluids can be represented by the following equation:

$$\varphi_v = \frac{\varphi_m}{\rho_p \left(\frac{\varphi_m}{\rho_p} + \frac{1-\varphi_m}{\rho_0} \right)} \quad (1)$$

2.3. *Experimental Methods*

The X-ray diffraction patterns of nanoparticles were measured in the $20-90^\circ$ 2θ range with a step size of about 0.015° and collection time of 250 s/step using a monochromatized (Cu K α 1, $\lambda = 1.5406 \text{ \AA}$) Bruker D8 Advance diffractometer equipped with a fast LynxEye detector. The powder X-ray diffraction patterns were refined by the Rietveld method [31] using the FullProf software [32], enabling the quantification of the phases in presence. The fitting of the peak broadening using a Thompson-Cox-Hasting function enables the deconvolution of the instrumental (determined from a corundum standard sample) and sample contributions to the broadening [33].

A Micromeritics Gemini VII 2390t instrument using a mixture of N₂/He (30%/70%) was used to experimentally evaluate from nitrogen physisorption the (BET) specific surface area of TiO₂ nanoparticles. Before BET measurement, all the tested samples were previously outgassed under vacuum at 100°C in order to avoid the nanoparticle surface hydration.

Scanning electron microscopy (SEM) characterization of the different types of TiO₂ nanoparticles was carried out with JEOL-JSM-7100F (JEOL USA Inc., Peabody, USA) equipment operating at 10 kV coupled with energy dissipative X-ray spectrometer (EDS) for

chemical composition evaluation of powder. Powder samples were deposited on a carbon adhesive tape substrate then submitted to carbon metallization under vacuum before to be tested.

To evaluate the electrical conductivity of nanofluids, a conductivity meter MultiLine 3630 (WTW GmbH, Weilheim, German) coupled with conductivity probe TetraCon 925 (for high conductive samples) and LR925/01 (for low conductive samples) (WTW GmbH, Weilheim, German) were used. The accuracy of the used conductivity probe was evaluated elsewhere, and it is 1% and 2% for TetraCon 925 [34] and LR925/01 [35] respectively. For temperature control and stabilization self-made system was made. The detailed description of whole measuring station can be found elsewhere in [36]. All measurements were conducted without undue delay directly after sample preparation in a temperature range from 10 to 45 °C (283.15–318.15 K) with 5 °C step and the accuracy of temperature stabilization was 0.2. The measurements for each temperature were conducted at least during 10 minutes and the average value was taken as an electrical conductivity for specific temperature.

3. Results and discussion

3.1. TiO_2 nanoparticles

The refined powder X-ray diffraction pattern of the different types of TiO_2 nanoparticles are presented in the Fig. 2. XRD experiments and data of Table 2 revealed that TiO_2 A nanoparticles are well made of anatase phase, and that average crystallite size is close to the average size of nanoparticles while the nanoparticles appears mainly aggregated in SEM characterization. Contrary to manufacturer specification, the Table 2 shows that TiO_2 M1 is mainly composed of nanoparticles with anatase phase while pure rutile was expected. In addition, TiO_2 M2 nanoparticles are dominated by rutile phase. Average crystallite sizes of TiO_2 M2 nanoparticles agree with average size of nanoparticles reported by the manufacturer. With TiO_2 M1, the average crystallite sizes of nanoparticles is 10 times higher than average nanoparticle size given by the manufacturer but agree with SEM characterization.

Figure 2: Rietveld refined powder X-ray diffraction pattern of TiO_2 a) anatase, b) rutile, c) mixture and their scanning electron microscopy images. The experimental data are plotted as red

symbols, the calculated pattern as black line and their difference as lower blue line. The vertical ticks indicate the Bragg peak positions of (up) the rutile phase ($P4_2/mnm$ space-group) and (down) the anatase phase ($I4_1/amd$ space-group).

Table 2: Main parameters obtained from the Rietveld refinements of the different TiO_2 samples

The (BET) specific surface area of TiO_2 nanoparticles was determined to 3.51 ± 0.08 m^2/g , 38.3 ± 0.2 m^2/g and 51.9 ± 0.2 m^2/g for TiO_2 A, TiO_2 M1 and TiO_2 M2 powder sample respectively.

SEM pictures of TiO_2 nanoparticles are reported in Fig. 2. This figure shows that anatase particle (TiO_2 A) are mainly in form of dense aggregates of several μm , while TiO_2 M1 and TiO_2 M2 nanoparticles are separate, near spherical and with similar average diameter of about 100 nm.

EDS spectroscopy of the TiO_2 nanoparticles is depicted in Figure 3. It shows that TiO_2 samples are mainly composed of Ti and O as expected but they also contain some other species. The presence of Al is noticed with TiO_2 A and TiO_2 M2 samples. Many different other species appear in TiO_2 M1 sample that makes this sample not strictly pure. It should be finally denoted that several EDS spectra have been taken in different locations for all the samples, and similar spectra were obtained.

Figure 3: Energy dispersive X-ray spectroscopy (EDS) spectra of a) TiO_2 A, b) TiO_2 M1, c) TiO_2 M2.

3.2. *Electrical properties of TiO_2 -EG nanofluids*

Effect of TiO_2 nanoparticles characterized by various phase (anatase and mixture of anatase and rutile) and temperature on electrical conductivity of ethylene glycol was investigated and results are presented in Figure 4, as well summarized in Table A.6. The graphs clearly show that addition of titanium dioxide nanoparticles, even in small amount and irrespective of their

phase, contributes to increase the electrical conductivity of base fluid, what was also reported elsewhere [13, 23, 24, 27, 26, 28, 29]. The scale of observed changes in electrical conductivity of various titanium dioxide-ethylene glycol nanofluids are different and depends on the average size of nanoparticles or phase of used TiO_2 nanoparticles and their ratios.

In this study, the most significant increase in electrical conductivity was observed for nanofluids with TiO_2 particles in anatase phase (TiO_2 A) with declared average particle size of 4-8 nm (Fig. 4, Table A.6). The highest value of electrical conductivity was noted for the highest tested content of TiO_2 A nanoparticles (20 wt.%) in ethylene glycol at 318.15 K and it was $10728 \mu\text{S}/\text{cm}$. On the other hand, the highest enhancement in comparison to base fluid in the same temperature was observed for 20 wt.% at 283.15 K. In this case a 4586458% enhancement was observed, for comparison at highest tested temperatures (318.15 K) it reaches 3461838%. According to the best author knowledge, such an increase is the highest measured for nanofluids containing titanium dioxide nanoparticles and one of the highest for ethylene glycol based nanofluids. Other two types of nanofluids also present enhancement in electrical conductivity with increasing content of nanoparticles, but in their case observed increase is much lower than that case of TiO_2 anatase nanoparticles. This difference can be caused by the nature of the anatase phase of TiO_2 , which researchers [37] show has better electrical properties than that rutile phase. For the nanofluids containing TiO_2 M1 nanoparticles where 93% is in anatase phase also occurs significant increase in electrical conductivity with increasing mass fraction of nanoparticles. The highest enhancement, again was observed for the lowest tested temperatures at highest mass fraction and it was 154242%. The highest increase for TiO_2 M2-EG nanofluid was observed at the same conditions and the enhancement was 8616%. The main differences between used nanoparticles is in the anatase phase. Obtained results allow to conclude that the higher content of anatase phase the higher electrical conductivity on nanofluid can be achieved.

Figure 4: The electrical conductivity of various type of titanium dioxide nanofluids (a) TiO_2 A-EG, (c) TiO_2 M1-EG (e) TiO_2 M2-EG and their enhancement (b) TiO_2 A-EG, (d) TiO_2 M1-EG (f) TiO_2 M2-EG.

As it was reported earlier, an increase in electrical conductivity of nanofluids can be caused mainly by two factors, namely (a) variation of electrical double layer (EDL) [13, 23] and (b) creating conduction paths at higher concentrations of nanoparticles [38] or their combination. The size of EDL is strictly related with Debye length and nanoparticles size, and the greater size of EDL the greater bulk electrical conductivity. In case of titanium dioxide ethylene glycol nanofluids it seems to that also the phase of used TiO_2 particles has an impact and in this context the anatase phase is favourable.

Data presented in this paper have also been compared to some theoretical models and numerical constellations proposed by other researchers. There were many attempts to develop theoretical models of electrical conductivity or improve the existing. The Maxwell model (2) is largely used in the literature, in most cases, it underestimates the experimental data:

$$\sigma_{nf} = \left(1 + \frac{3(\alpha - 1)\varphi_v}{(\alpha + 2) - (\alpha - 1)\varphi_v} \right) \sigma_{bf}, \quad (2)$$

where $\alpha = \sigma_p / \sigma_{bf}$. This is because the Maxwell model concerns only volume fraction, electrical conductivity of base fluid and particles [24, 27]. Additionally, it assume that particles are spherical, randomly arranged and distance between them is considerably larger than their diameter so it is applicable only for low concentrations [39]. It does not take into account factors such as (a) Brownian motion, (b) EDL, (c) nanoparticles size, and (d) specific surface area, which can affect on electrical properties of nanofluids. According the best authors knowledge there is only one case where Maxwell model does not differ much from experimental data and it was presented by Sarojini et al. [40] for copper-water and copper-ethylene glycol nanofluids.

Cruz et al. [39] proposed to simplify the Maxwell model for three cases: (a) when conductivity of particles is much lower than base fluid:

$$\sigma_{nf} = \left(1 - \frac{3}{2} \varphi_v \right) \sigma_{bf}, \quad (3)$$

(b) when conductivity of particles is comparable to conductivity of base fluid:

$$\sigma_{nf} = \sigma_{bf}, \quad (4)$$

(c) when conductivity of particles is much higher than base fluid:

$$\sigma_{nf} = (1 + 3\varphi_v) \sigma_{bf}. \quad (5)$$

The behaviour of electrical conductivity for nanofluid with dispersed TiO_2 nanoparticles

was described by Awin et al. [13]. They proposed the following equation which takes account volume fraction and temperature in range from 0.0015 to 0.005% and 25 to 45 °C respectively:

$$\sigma_{nf} = 0.459T^{0.968}\phi_v^{0.24}. \quad (6)$$

Also Chereches and Minea [24] proposed a formula for electrical conductivity of titanium dioxide nanofluid, which was obtained by numerical fitting with coefficient $R^2 = 0.94$ at ambient temperature and volume fraction between 1 and 3%:

$$\sigma_{nf} = 388.11\phi_v + 337.29, \quad (7)$$

where ϕ_v is the nanoparticle volume concentration expressed in %. They also present regression equation for titanium dioxide water nanofluid in volume concentration range of 1-3% and temperature between 20-60 °C:

$$\sigma_{nf} = 491.56 + 104.67\phi_v + 71.37\phi_v^2 + 4.19T. \quad (8)$$

An equation for electrical conductivity of titanium dioxide water ethylene glycol nanofluids were also introduced by Islam et al. [28]:

$$\sigma_{nf} = (11.214 + 2.626\ln\phi_v + 0.2371\ln T)\sigma_{bf}. \quad (9)$$

The comparison of previous equations and numerical fittings to obtained results are presented in Fig. 5. For this purpose, the experimental data of the three types of titanium dioxide nanofluids at 25 °C (298.15 K) were presented as electrical conductivity as a function of volume concentration Fig. 5 (a) and volume fraction Fig. 5 (b). Results are presented in both volume fraction and volume concentration. A comparative analysis of experimental data and theoretical and numerical models published previously show significant discrepancy. The classical model such as Maxwell and its simplification proposed by Cruz show very high underestimations, as well as the correlation proposed by Islam et al. [27]. Also, functions proposed by Chereches and Minea are not suitable for predicting the electrical conductivity of any of the titanium dioxide nanofluid presented in this study. For TiO_2 -A-EG show large underestimates, while for the other two they strongly overestimate. The observed discrepancy between experimental data and models is caused by previously mentioned imperfections of assumptions of the used models and correlations, such as taking into account only the load of nanoparticles and their electrical conductivity.

Figure 5: The comparison of theoretical model and numerical fittings to experimental data at 25 °C for data and models presented in (a) volume fraction , and (b) volume concentration . Points are for experimental data and solid lines are fitting functions or theoretical models.

The experimental data presented in this paper have also been numerically analysed and the evolution of electrical conductivity of titanium dioxide ethylene glycol nanofluids can be described with good accuracy by the following power function:

$$\sigma_{nf} = (1 + B\varphi_m^A) \sigma_{bf}. \quad (10)$$

Consequently, the enhancement in EC can be expressed by following equation:

$$\frac{\sigma_{nf}}{\sigma_{bf}} = 1 + B\varphi_m^A, \quad (11)$$

where A and B are numerical factors. The fitting was performed with OriginPro software with R^2 better than 0.997 for TiO_2 A-EG, TiO_2 M1-EG and 0.928 for TiO_2 M2-EG nanofluids. The results of the fitting can be seen in Figure 6 where experimental data and obtained functions were presented.

Figure 6: The electrical conductivity of various type of titanium dioxide nanofluids (a) TiO_2 A-EG, (c) TiO_2 M1-EG (e) TiO_2 M2-EG and their enhancement (b) TiO_2 A-EG, (d) TiO_2 M1-EG (f) TiO_2 M2-EG. Dots represents experimental data and solid lines are fitting functions, lines colour correspond to temperature presented by dots with the same colour.

For evidencing the relevance of the power function to describe experimental results of electrical conductivity obtained by other researchers, equation (10) was applied to experimental data obtained by Sikdar et al. for titanium dioxide nanoparticles dispersed in water, which can be seen in Fig. 7. Fitting was performed with OriginPro software with $R^2 = 0.9638$.

Figure 7: The ability of the proposed power-law function to describe experimental results obtained by Sikdar et al. [25]

The conductivity data analysis was based on power function introduced in relation (11).

Prescribed normalization reduces the complexity of problem as all thermal dependent factors purely related to the base fluid are included in the corresponding denominator. Further all values on the right hand side of equation (11) were shifted. This procedure was realized by introducing a normalized conductivity σ_N defined by a simple substitution:

$$\sigma_N = \frac{\sigma_{nf}}{\sigma_{bf}} - 1. \quad (12)$$

Finally the power law of equation (11) was rewritten in a form:

$$\sigma_N = B\varphi_v^A. \quad (13)$$

Further simplification was possible since the equation (13) is linearizable:

$$\log(\sigma_N) = A\log(\varphi_v) + \log(B), \quad (14)$$

where the coefficients A and B and the corresponding uncertainties $u(A)$ and $u(B)$ was calculated using the linear regression model. The normalized conductances σ_N plotted in Fig. 8 are in good correspondence with relation (14) and creates relationship close to linear. To confirm this statement all the fitting details for each sample was presented in Tables 3-5, where it can be seen that A coefficients for each type of sample take similar values. The calculated coefficient of determination for the samples TiO_2A-EG and TiO_2M1-EG are above 99%, $R^2 > 0.99$ and for the remaining one is not less than 0.96. This observation suggests that it may be sufficient to assume that the power of concentration is temperature independent. However this statement needs further investigations of experimental data.

Table 3: Fitting parameters with corresponding coefficients of determination for the TiO_2 A-EG nanofluids

Table 4: Fitting parameters with corresponding coefficients of determination for TiO_2 M1-EG nanofluids

Table 5: Fitting parameters with corresponding coefficients of determination for TiO_2 M2-EG nanofluids

4. Conclusions

The electrical conductivity of three various type of titanium dioxide ethylene glycol nanofluid were investigated. The samples were prepared by two-step method with mass fraction range from 0.01 to 0.20. The obtained results show increase in electrical conductivity with the content of TiO_2 nanoparticles in ethylene glycol, and it power is dependent on phase composition of TiO_2 nanoparticles. The most significant enhancement was noted for nanofluids containing titanium dioxide with pure anatase phase and it was over 4586400% at 10 and 20 wt.%. Also $\text{TiO}_2\text{M1-EG}$ nanofluids are characterized by quite high increase in electrical conductivity at the same conditions. On the other hand, the lowest TiO_2 nanoparticles effect was observed for samples where the prevailing phase was rutile. It allows to conclude that anatase phase is favourable for electrical conductivity enhancement. The experimental results were also compared with available models and theoretical correlations. It was concluded that there is no consistent with those models and new one was proposed for the investigated nanofluids.

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Appendix A. The electrical conductivity of the different TiO_2 -EG nanofluids

Table A.6: The electrical conductivity of the different TiO_2 -EG nanofluids

Appendix B. Numerical analysis of experimental data

Figure 8: Linearised datasets of normalized conductivity σ_N as a function of concentration for different temperatures.

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Table 1: Summary of electrical properties of TiO₂ nanofluids with various base fluids.

| Base fluid | Nanoparticles size (nm) | Nanoparticles load | | Electrical conductivity range (μS/cm) | Temperature range (°C) | Preparation method | Ref. |
|------------|-------------------------|--------------------|------------|---------------------------------------|------------------------|--|------|
| W | 10-20 | 0.0015 | 0.005 vol% | 2.3 - 5* | 25-45 | 2-step, various sonication time (30-180 min) | [13] |
| W | 13.5 | 0.25* - 4 vol% | | 8876%† | 25 | - | [23] |
| W | - | 1 - 3vol% | | 26 - 1500* | 20-60 | dilutions | [24] |
| W | 20-30 | 0.5 - 3.0 vol% | | 3-275 | 24-45 | 2-step | [25] |
| W/EG | 40 | 0.05 - 0.5 vol% | | 5-65* | 50 | 2-step, 1h sonication | [26] |
| W/EG | - | 0.05 - 0.5 vol% | | 20 - 77* | 20 - 70 | 2-step | [27] |
| W/EG | 40 | 0.05 - 0.5 vol% | | 5-77* | 20-70 | 2-step | [28] |
| EG | 20 | 0.05 - 1.0 wt% | | 2-75* | 30-90 | 2-step, 1h sonication | [29] |
| O | 47 | 0.1wt. % | | 0.5* | 20 - 45 | 2-step, 1h sonication | [30] |

*data read from graph, † authors gives only enhancement of electrical conductivity.

Table 2: Main parameters obtained from the Rietveld refinements of the different TiO₂ samples

| Sample Name | Phase in presence | Cell parameters | Phase proportion | Average crystallite size |
|-----------------------|----------------------|--------------------------------|------------------|-----------------------------|
| [-] | [-] | [Å] | [wt.%] | [Å] |
| TiO ₂ (A) | anatase | a = 3.796(2) c = 9.508(4) | 100 | 31 |
| TiO ₂ (M1) | anatase | a = 3.7867(1) c = 9.5105(3) | 93 | 203 |
| | rutile | a = 4.5948(3) c = 2.9580(4) | 7 | 250 |
| TiO ₂ (M2) | anatase | a = 3.7869(1) c = 9.5111(3) | 10 | 185 |
| | rutile | a = 4.5954(3) c = 2.9608(3) | 90 | 286 |

Table 3: Fitting parameters with corresponding coefficients of determination for the TiO₂A-EG nanofluids

| T | A | $u(A)$ | B | $u(B)$ | R^2 |
|----|---------|---------|---------|---------|---------|
| 10 | 0.83862 | 0.01274 | 5.61289 | 0.02371 | 0.99867 |
| 15 | 0.83946 | 0.01243 | 5.56246 | 0.02314 | 0.99869 |
| 20 | 0.84218 | 0.01197 | 5.57273 | 0.02228 | 0.99879 |
| 25 | 0.84172 | 0.01067 | 5.55205 | 0.01987 | 0.99904 |
| 30 | 0.84532 | 0.01164 | 5.54980 | 0.02167 | 0.99886 |
| 35 | 0.85255 | 0.01294 | 5.55678 | 0.02408 | 0.99862 |
| 40 | 0.84401 | 0.01027 | 5.52911 | 0.01911 | 0.99911 |
| 45 | 0.84119 | 0.00966 | 5.49884 | 0.01799 | 0.99921 |

Table 4: Fitting parameters with corresponding coefficients of determination for TiO₂M1-EG nanofluids

| T | A | $u(A)$ | B | $u(B)$ | R^2 |
|----|---------|---------|---------|---------|---------|
| 10 | 0.85236 | 0.01299 | 4.22384 | 0.02482 | 0.99861 |
| 15 | 0.85267 | 0.01268 | 4.18038 | 0.02314 | 0.99868 |
| 20 | 0.85580 | 0.01214 | 4.20137 | 0.02321 | 0.99879 |
| 25 | 0.85632 | 0.01159 | 4.19586 | 0.02215 | 0.99890 |
| 30 | 0.85547 | 0.01055 | 4.19862 | 0.02017 | 0.99909 |
| 35 | 0.85840 | 0.00995 | 4.21429 | 0.01903 | 0.99919 |
| 40 | 0.85841 | 0.00858 | 4.21183 | 0.01640 | 0.99940 |
| 45 | 0.86041 | 0.00945 | 4.20579 | 0.01806 | 0.99928 |

Table 5: Fitting parameters with corresponding coefficients of determination for TiO₂M2-EG nanofluids

| T | A | $u(A)$ | B | $u(B)$ | R^2 |
|-----|---------|---------|---------|---------|---------|
| 10 | 0.60705 | 0.03992 | 2.57075 | 0.07631 | 0.97471 |
| 15 | 0.60336 | 0.03981 | 2.53207 | 0.07610 | 0.97454 |
| 20 | 0.51690 | 0.04120 | 2.42253 | 0.07875 | 0.96329 |
| 25 | 0.56828 | 0.03831 | 2.49895 | 0.07323 | 0.97346 |
| 30 | 0.57550 | 0.03555 | 2.52454 | 0.06796 | 0.97761 |
| 35 | 0.56935 | 0.03021 | 2.53563 | 0.05775 | 0.98339 |
| 40 | 0.57478 | 0.02866 | 2.55945 | 0.05479 | 0.98530 |
| 45 | 0.57443 | 0.02584 | 2.56797 | 0.04940 | 0.98800 |

Table A.6: The electrical conductivity of the different TiO₂-EG nanofluids

| Sample Name | φ_m | electrical conductivity, $\mu S/cm$ | | | | | | | |
|-----------------------|-------------|-------------------------------------|----------|----------|----------|----------|----------|----------|----------|
| | | 283.15 K | 288.15 K | 293.15 K | 298.15 K | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
| | 0.000 | 0.08 | 0.11 | 0.13 | 0.16 | 0.19 | 0.22 | 0.26 | 0.31 |
| TiO ₂ (A) | 0.010 | 257.08 | 313.67 | 374.62 | 441.61 | 514.92 | 592.84 | 678.00 | 765.06 |
| | 0.020 | 466.02 | 562.77 | 668.91 | 783.38 | 901.94 | 970.29 | 1175.36 | 1316.95 |
| | 0.030 | 619.54 | 753.51 | 900.00 | 1054.87 | 1221.83 | 1412.15 | 1602.17 | 1814.12 |
| | 0.040 | 801.47 | 976.12 | 1178.53 | 1384.08 | 1613.43 | 1853.38 | 2110.72 | 2391.87 |
| | 0.050 | 931.02 | 1139.92 | 1379.28 | 1627.05 | 1890.90 | 2180.31 | 2512.96 | 2818.39 |
| | 0.100 | 1778.47 | 2155.67 | 2568.49 | 3047.14 | 3549.35 | 4086.71 | 4672.46 | 5250.95 |
| | 0.150 | 2702.32 | 3283.02 | 3958.32 | 4672.57 | 5436.00 | 6273.17 | 7110.17 | 8014.18 |
| | 0.200 | 3669.17 | 4490.34 | 5402.31 | 6283.77 | 7409.00 | 8491.03 | 9650.83 | 10727.98 |
| TiO ₂ (M1) | 0.010 | 8.44 | 10.50 | 12.91 | 15.55 | 18.71 | 22.11 | 25.95 | 30.46 |
| | 0.020 | 14.60 | 18.10 | 22.06 | 26.95 | 32.50 | 38.46 | 45.61 | 52.54 |
| | 0.030 | 22.29 | 27.49 | 33.62 | 40.75 | 48.74 | 57.65 | 67.59 | 78.52 |
| | 0.040 | 29.51 | 36.60 | 44.82 | 54.14 | 64.77 | 76.50 | 89.57 | 104.48 |
| | 0.050 | 36.22 | 44.63 | 54.44 | 66.12 | 78.97 | 93.59 | 109.25 | 126.89 |
| | 0.100 | 65.60 | 81.50 | 99.65 | 121.65 | 145.48 | 172.29 | 203.39 | 236.84 |
| | 0.150 | 92.91 | 116.83 | 143.79 | 174.54 | 210.03 | 249.58 | 293.05 | 342.61 |
| | 0.200 | 123.39 | 151.65 | 188.57 | 227.48 | 272.90 | 326.39 | 384.02 | 451.21 |
| TiO ₂ (M2) | 0.010 | 0.92 | 1.16 | 1.91 | 1.80 | 2.19 | 2.67 | 3.18 | 3.85 |
| | 0.020 | 1.37 | 1.78 | 2.30 | 2.92 | 3.53 | 4.26 | 5.19 | 6.20 |
| | 0.030 | 1.70 | 2.21 | 2.83 | 3.76 | 4.41 | 5.32 | 6.47 | 7.77 |
| | 0.040 | 1.86 | 2.37 | 3.58 | 3.75 | 4.63 | 5.77 | 7.09 | 8.98 |
| | 0.050 | 2.25 | 2.94 | 3.71 | 4.65 | 5.74 | 7.11 | 8.61 | 10.52 |
| | 0.100 | 3.09 | 3.92 | 4.92 | 6.02 | 7.43 | 9.15 | 11.41 | 13.99 |
| | 0.150 | 4.19 | 5.30 | 6.60 | 8.02 | 9.84 | 12.01 | 14.63 | 17.82 |
| | 0.200 | 6.89 | 8.67 | 10.11 | 12.38 | 15.22 | 17.83 | 21.66 | 25.85 |

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Jacek Fal: Conceptualization, Methodology, Investigation, Formal analysis, Writing - Original Draft, Visualization, Writing - Review & Editing
Jolanta Sobczak: Data Curation, Investigation
Ryszard Stagraczyński: Formal analysis, Visualization
Patrice Estellé: Investigation, Validation, Writing - Review & Editing
Gawel Żyła: Validation, Writing - Review & Editing, Supervision

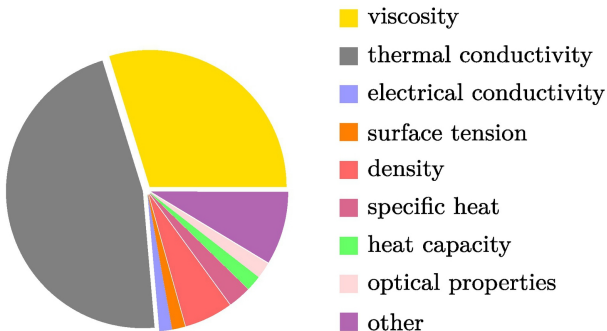
Highlights

The electrical conductivity of titanium dioxide ethylene glycol was investigated.

A significant increase in the electrical conductivity of nanofluids was observed.

Crystalline phase effect on electrical conductivity of TiO₂-EG nanofluids was shown.

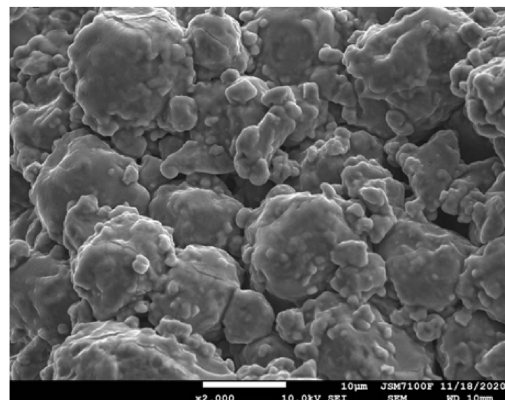
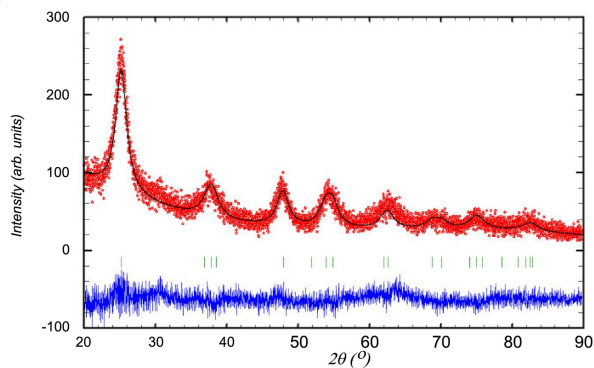
The new correlation of electrical conductivity of TiO₂-nanofluids was introduced.



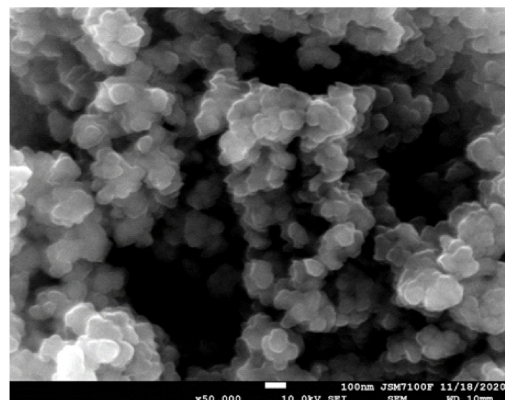
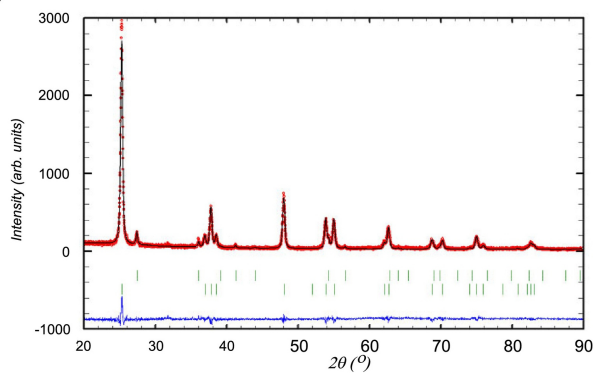
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Figure 1

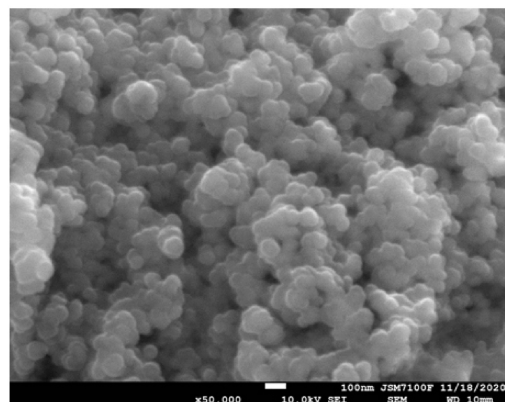
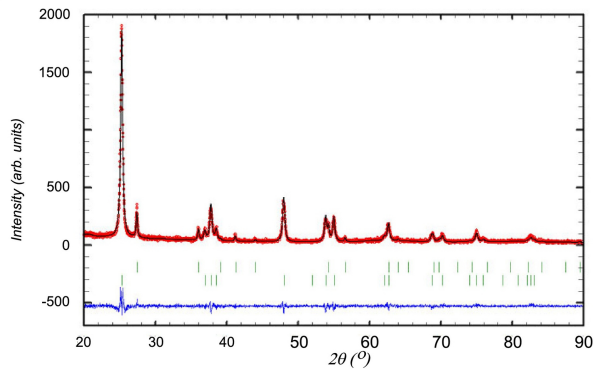
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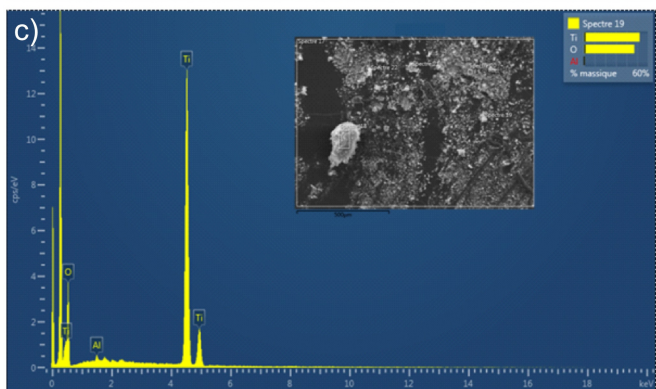
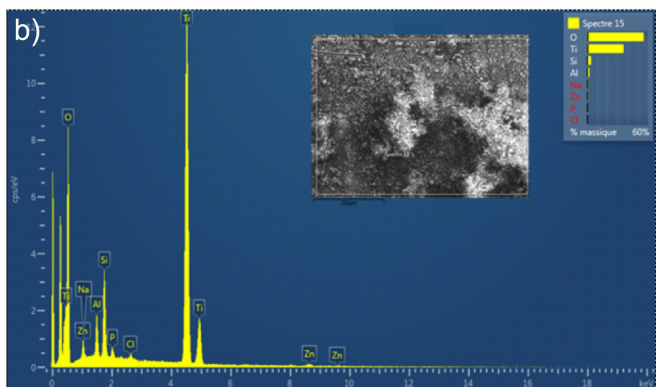
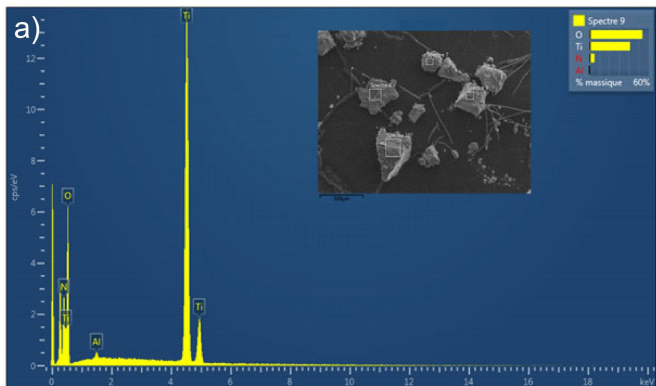


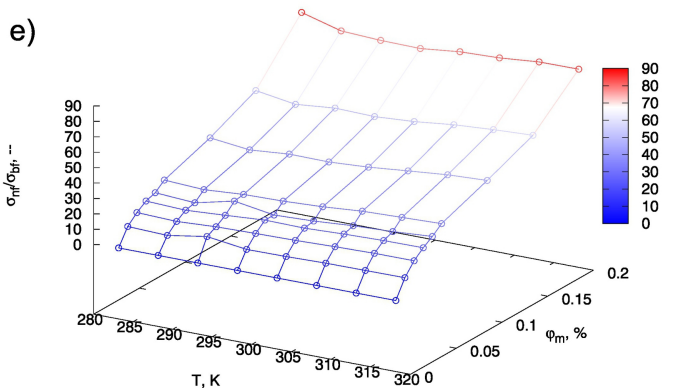
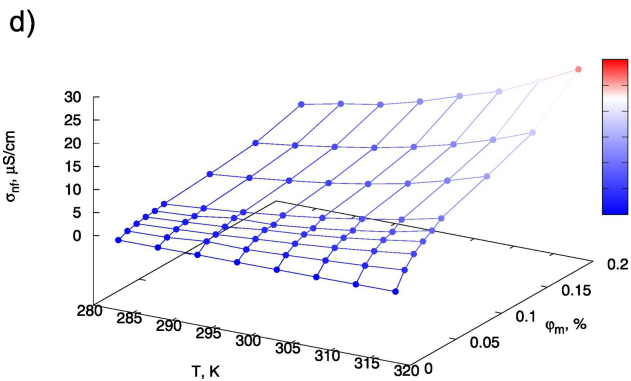
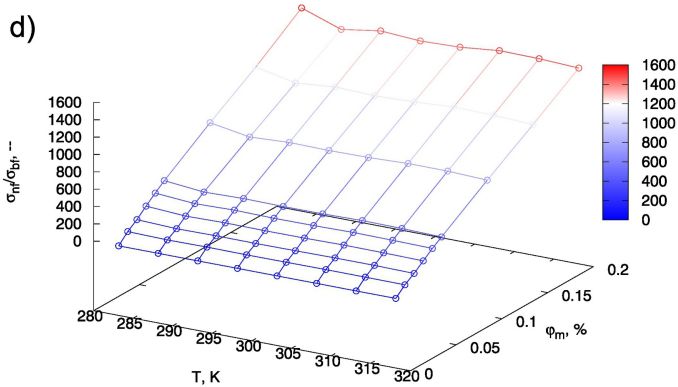
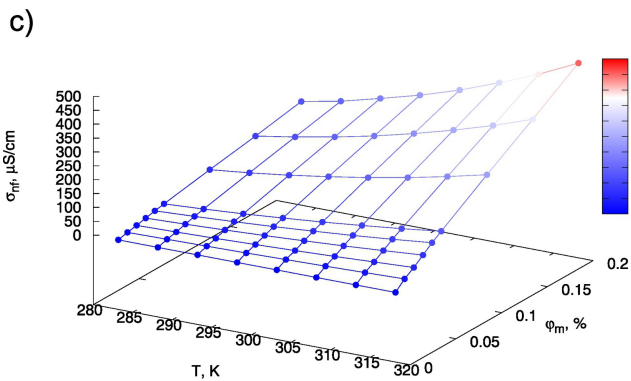
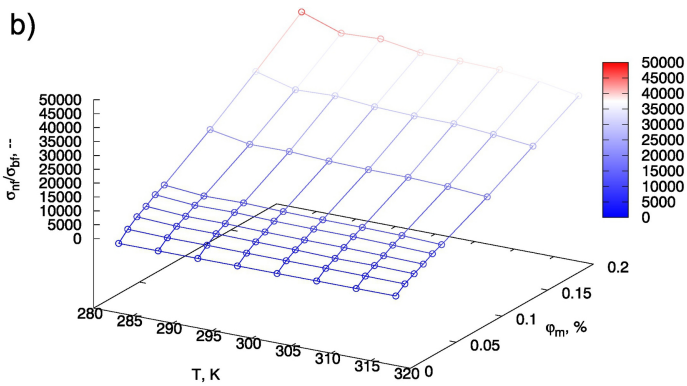
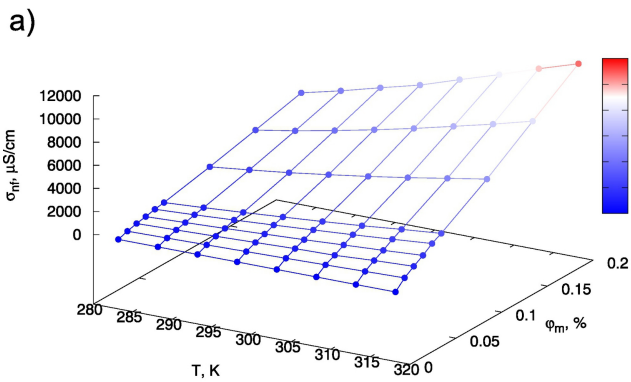
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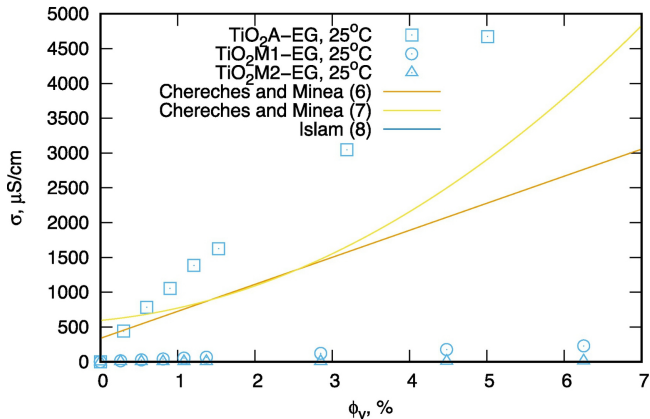
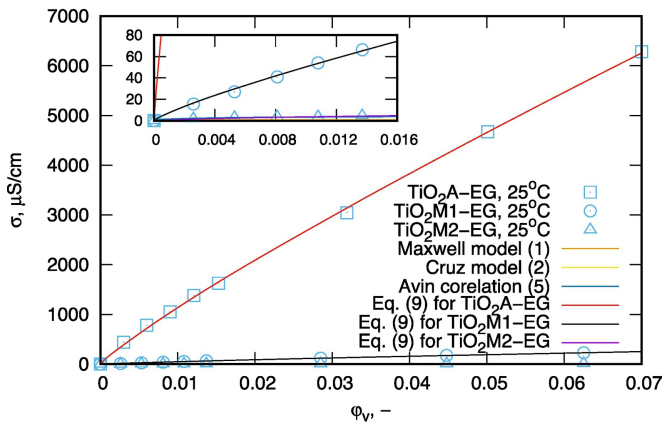


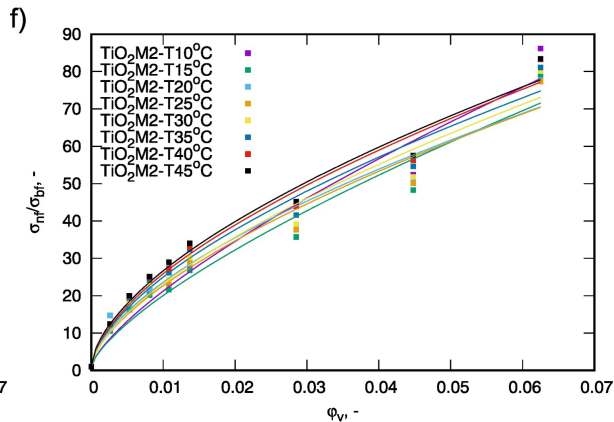
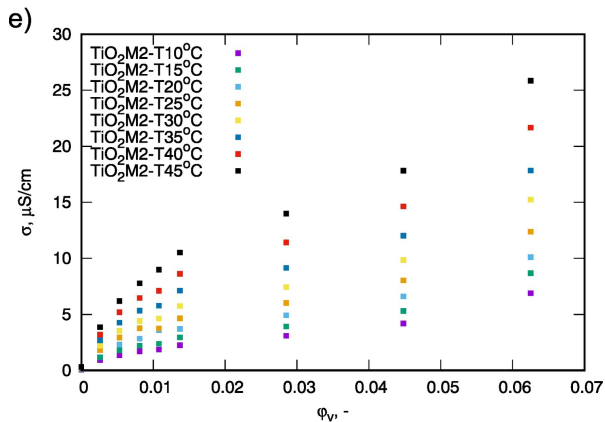
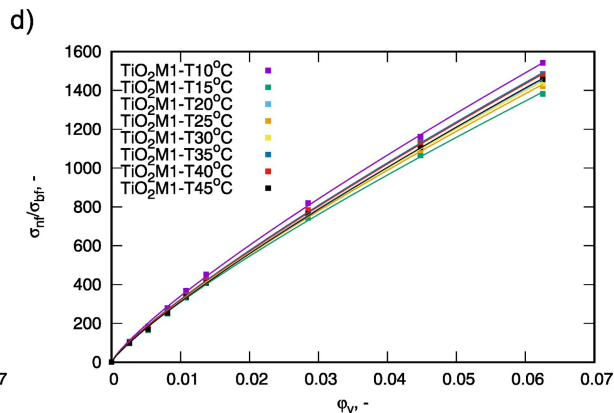
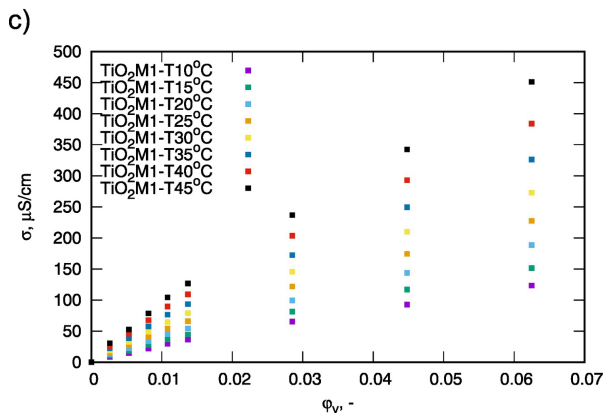
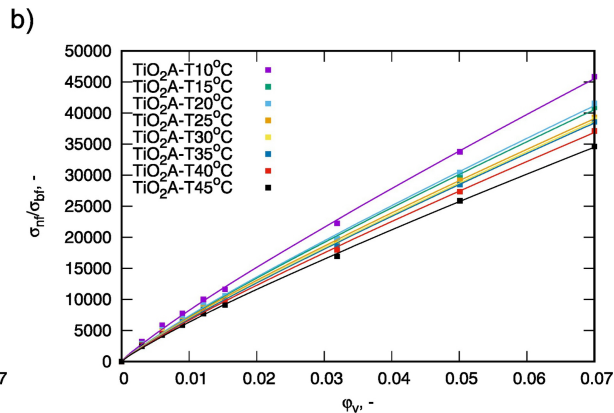
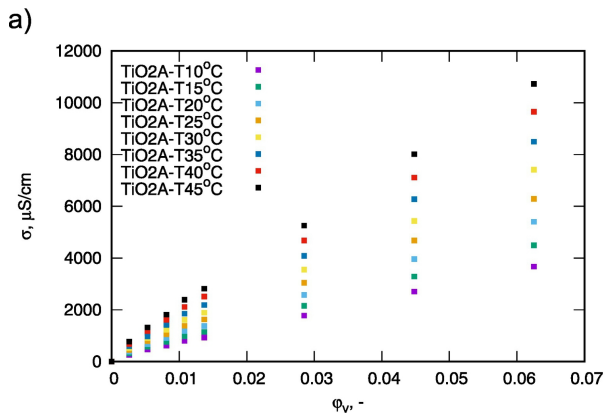
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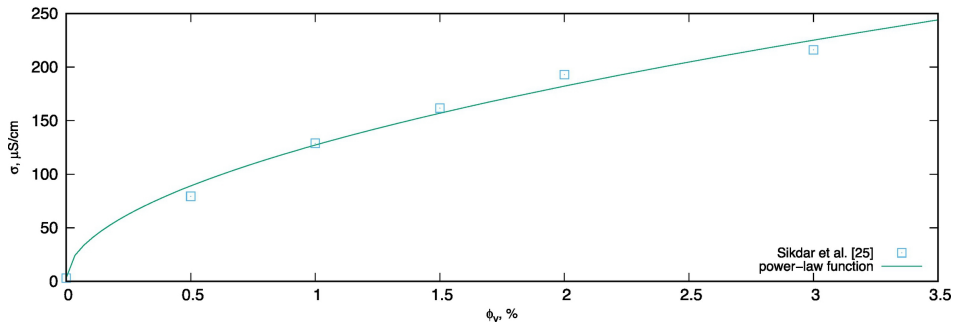
Figure 2











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Figure 7