1. Oleksandr BOIKO[1], 2. Radosław GAD[1], 3. Makiko KOBAYASHI[2], 4. Fumiaki MITSUGI[2], 5. Illia DIAHOVCHENKO[3]

Lublin University of Technology, Department of Electrical Engineering and Superconducting Technologies (1)
Kumamoto University, Faculty of Advanced Science and Technology (2)
Sumy State University, Electric Power Engineering Department (3)
ORCID: 1. 0000-0001-7759-6269; 2. 0000-0002-9042-4346

doi:10.15199/48.2024.08.22

Nanofluids containing conductive nanoparticles: the review of thermal and electrical properties. Selected applications in electrical and thermal engineering, and energy sector

***Abstract**. This paper presents a brief review of the thermal and electrical properties of nanofluids containing metallic, metallic oxide, graphene nanoparticles, as well as carbon nanotubes. The key factors, such as the alignment of magnetic NPs, NPs size and shape, pH of the base fluid, surfactants, solvents, temperature, base fluid, and NPs types, that demonstrate a significant impact on the thermo-electrical properties of nanofluids are analyzed. The applications of nanofluids in transformers (oil, cores, paper impregnation), PVT systems, and hydrogen production are described.*

***Streszczenie.** W pracy przedstawiono przegląd właściwości termicznych i elektrycznych nanocieczy zawierających metale, tlenki metali, nanocząstki grafenu oraz nanorurki węglowe. Przeanalizowano kluczowe czynniki, takie jak ustawienie magnetycznych cząstek, ich wielkość i kształt, pH płynu bazowego, środki powierzchniowo czynne, rozpuszczalniki, temperatura, rodzaje cząstek i płynów, które wykazują znaczący wpływ na właściwości termoelektryczne nanocieczy. Opisano zastosowania nanocieczy w transformatorach, układach PVT i produkcji wodoru. (**Nanofluidy zawierające przewodzące nanocząsteczki: przegląd właściwości cieplnych i elektrycznych. Wybrane zastosowania w elektrotechnice i inżynierii cieplnej oraz sektorze energetycznym**)*

Keywords: nanofluids, nanoparticles, base fluids, thermoelectrical properties.
Słowa kluczowe: nanociecze, nanocząstki, płyny bazowe, właściwości termoelektryczne.

Introduction

One of the most important factors determining the development of society, science, and technology is the efficiency of transmitting and storing energy in any form. Modern methods of energy transport and accumulation have reached such an advanced level that any improvement in their effectiveness is only possible by returning to fundamental research. Nanofluids (NFs), also known as suspensions of nanoparticles (NPs) in a base fluid (BF), have the potential to become a breakthrough solution due to their significantly better properties, e.g., thermal, optical and magneto-electric, than the conventional macroscopic equivalents of their individual components [1-3]. In addition, the configuration of nanofluids containing metallic NPs in the volume of a dielectric liquid as well as metal-dielectric thin film structures [4-6] or nanostructured coatings [7], are almost ideal structures for studying electrical transport, dielectric polarization, and relaxation processes because they allow the study of electric charge transfer both between individual metal NPs and between NPs and large conducting agglomerations.

The paper presents a brief discussion on the thermal and electrical properties of nanofluids containing metallic (especially magnetic) nanoparticles randomly dispersed in different types of BFs. The greatest attention will be given to the electrical properties and application of NFs in the electrical engineering and energy industries.

Nanofluids manufacturing

Production of nanofluids is an extremely important process because it must complete all of the requirements, allowing further either laboratory or industrial applicability. During the synthesis, the solid, or in the form of a nanodroplet, metallic or metallic oxide NPs are dispersed into base liquids such as water, ethylene glycol (EG), oils (mineral, silicon, vegetable), and other liquid polymers [8,9]. The manufactured NFs should demonstrate homogeneity and hydrodynamic stability of the suspension, as well as possibly low agglomeration or cluster formation of NPs, and chemical stability. Papers [10,11] suggest three methods for suspension stabilization: pH value manipulation, surface activators and/or dispersants directly used during the synthesis, and using ultrasonication. These methods allow for changes in the surface properties of the suspended NPs and a significant decrease in the number of cluster formations. The end-application of the NF decides about choosing a stabilization method.

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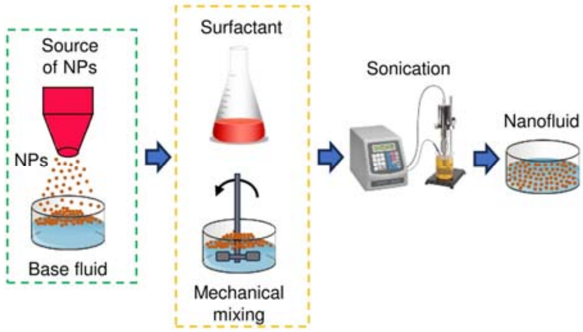

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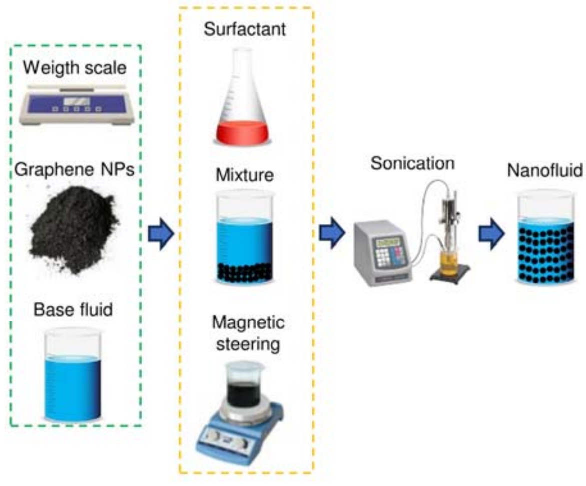


Fig.1. Schematic diagram of: a) one-step and b) two-step methods for NF production

All NF preparation methods can be divided into two groups: one-step (Fig. 1.a) and two-step (Fig. 1.b). In the one-step method, the NPs are produced and dispersed into the BF during the single preparation process.

For this purpose, in most cases, physical vapor deposition techniques such as evaporative deposition, laser ablation, magnetron sputtering, etc. that allow to produce uniform NPs are used [12-14]. The direct evaporation and condensation of NPs are carried out in the BF.

The two-step method relies on first producing the NPs in the form of nanopowder and then directly mixing them with the BF [15,16]. One of the main drawbacks of this method is NPs aggregation. That's why the common practice to solve the issue is using surfactants during mixing and ultrasonication after the NPs have been initially dispersed. The two-step method is considered to be the most economical and commercial type for large-scale NFs manufacturing. The majority of the different size nanopowders are commercially available and relatively inexpensive in comparison to single-step production.

Thermal properties of nanofluids

A significant number of papers on nanofluids just discuss the effects of suspensions with metallic nanoparticles on the enhancement of heat transfer in different engineering systems and devices. Most of them concern the influence of the parameters of nanofluid components on their thermal conductivity. The key parameters of nanofluids for thermal applications (also shown in Fig. 2) include: alignment of metallic (magnetic) nanoparticles, particle size and shape, pH of the fluids, surfactants, solvents, and hydrogen bonding, temperature, base fluid, type of the nanoparticles.

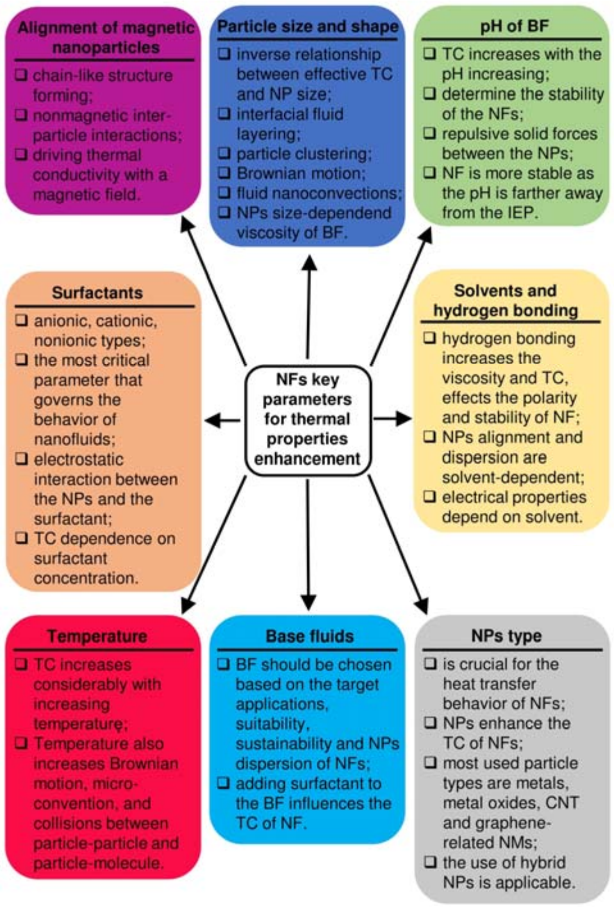


Fig.2. NF key parameters enhancing their thermal properties. TC – thermal conductivity, NM – nanomaterial

The nanofiller alignment in the BF is reported as a highly influential factor for NF thermal, electrical, and mechanical responses, especially in the case of samples containing carbon nanotubes (CNTs), graphene or reduced graphene oxides (GO), and magnetic NPs [17,18]. For example, after the application of the external magnetic field to the sample containing CNTs and mixing it with the magnetically sensitive Fe_2O_3 NPs, the resulting TC of the NF increased by about 30% [19]. The way more effect of magnetic field application to the Ni-coated CNT NFs was reported in [20], where the TC was increased by about 60%.

The effect of particle size and shape on heat transfer is one of the most disputed issues in the NF's scientific area. Despite the fact that there is a direct proportional relationship between particle size and the TC of the NFs [21], the inverse dependence of these characteristics is widely discussed [22]. In accordance with [22], the inverse relationship between effective TC and nanofiller's size can be explained by taking into account interfacial fluid layering, particle clustering, Brownian motion, and fluid nano-convections. The stationary and dynamic particle modeling shows that heat transfer in the NF is a surface phenomenon. A decrease in NP size causes an increase in the surface-to-volume ratio and an enhancement of interphase heat transfer afterwards [23].

pH demonstrates a sufficient impact on the TC and determines the stability of the NFs (mainly because of the creation of repulsive forces between NPs). The TC improvement in the NFs is strongly dependent on the isoelectric point (IEP) of the nanofiller. Itcan be explained by the DLVO theory presented in [24]. If the pH value is about IEP, there are no repulsive forces between the NPs, which means that they can easily agglomerate. This significantly decreases the suspension stability and lowers the TC. The farther the pH value is from the IEP, the more stable the NF is. Lower-pH NFs are characterized by more intense particle movement, which improves micro-convection and facilitates the heat transfer process [25].

The selection of surfactants is a crucial parameter that allows for the production of stable, homogeneous, and long-living NF. The basic types of surfactants for NFs are anionic, cationic, and nonionic [22]. In comparison to cationic surfactants, the nonionic group allows for good nanofiller alignment and dispersion in the BF. The anionic surfactants are widely used in the hybrid NFs in various BFs for TC studies. A study [26] shows that the TC of the hybrid NF increases when the surfactant concentration is increased. Moreover, higher BF viscosity leads to an improvement in TC. Using nonionic surfactants in CNT-NFs also significantly increases the heat transfer in NF, as presented in [27]. Selecting a surfactant is a very responsible and important stage in the NF's production; e.g., choosing the non-conductive surfactant decays the heat transfer and drastically drops the TC of the NF.

Some nanofillers can form chemical hydrogen bonds with the BF that can improve its viscosity and the NF's TC [28]. A strong correlation between NF's hydrogen bonding, polarity and viscosity, and dispersion, as well as the magnetic alignment of the Fe_2O_3 NPs, was reported in [29]. The study suggests that hydrogen bonding increases the viscosity of the NFs with multiple OH groups, which significantly hinders the NP's dispersion and alignment and leads to the enhancement of TC. Moreover, the hydrogen bonding also provides an enhancement in electrical conductivity, as is shown in the case of multiwalled CNTs in Krytox XHT750 oil [30].

The thermal treatment of NF has a critical effect on its thermal and electric properties. It is strictly related to the kinetic energy of the molecules, or NPs, that increases due to an increase in their movement in the BF. The Brownian motion, micro-convention, as well as interparticle and/or particle-molecule collisions, intensified when the temperature went up. The statement that the effective TC is a function of temperature was confirmed in the papers [31,32].

Base fluid selection is very important and crucial for the end-application of the NF. It should allow good alignment and dispersion of nanofiller, which will lead to enhanced thermal properties. With no doubt, the most widely used BF for the fabrication of NFs is water (distilled water), mainly because of the highest value of TC in comparison to other BFs such as EG, propylene glycol, engine, vegetable, and transformer oils, etc. [21]. In a number of cases, the more viscous BFs are mixed with water in order to reduce the viscosity of the solution and increase its initial TC [33]. At the same time, BFs with higher viscosity coefficients and relatively low TC at the end of production demonstrate better stability and a higher TC value [34].

Without a doubt, the selection of nanofiller as well as BF type is crucial for the physico-chemical properties of the NFs. The most widely used nanofillers are metals and their oxides, carbon- or CNT-contained materials, graphene and its oxide, etc. [35]. In the case of pure metals, Ag, Cu, Ni, and their oxides are commonly selected because of their oxidation resistance and chemical stability. Graphene and CNTs are widely used for TC enhancement of the NF [36]. In a number of cases, hybrid NFs where as a nanofiller two or more types of particles (or CNTs) are used, the synergetic effect of these NPs plays a key role in the thermal properties [37].

Electrical properties of conductive filler nanofluids

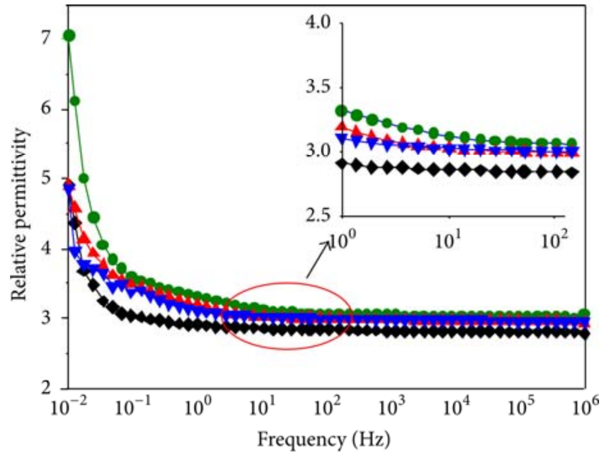
Taking into account that the most commonly used conductive nanofillers are pure or/and (hybrid type) oxidized metals, graphene and CNTs including them into the BFs, which normally are dielectric, significantly increases the electrical conductivity of the NF. The literature reports a lot of examples proving this fact. For example, mineral oil-based NFs contained Fe_3O_4 NPs; the resistivity of NF is about 10 times lower than in pure BF, and its dissipation factor rises while the concentration of Fe_3O_4 also increases [38]. The study [38] also suggests that the improved thermal properties of NFs (among others because of the addition of conductive NPs) contribute to the enhancement of their electric breakdown strength. Another study of Fe_3O_4 NPs in vegetable oil showed that there is an impact of the nanofiller's particle size on the dielectric properties of the NFs [39]. Fig. 3 demonstrates that an increase in NP size causes an increase in relative permittivity, especially for the frequencies of 0.01 Hz-100 Hz (Fig. 3.a). This range is also characteristic of dissipation factor dependency (Fig. 3.b); however, higher frequency ranges demonstrate a weak and insignificant size dependency. The paper also reports a weak frequency dependency of volume resistivity [39].

Fig. 4 presents the dependence of the DC conductivity of the $CaCO_3$-EG NFs on the nanofiller's mass fraction, which ranges from 0.01 to 0.03. It can be clearly seen that the conductivity increases with an increase in $CaCO_3$ concentration. The AC conductivity of NFs filled with $CaCO_3$ NPs and measured at different temperatures is more than 10 times higher in comparison to EG, as reported in [40].

A study [41] reports the great conductivity enhancement dependency on mass fraction (from the range of 0.0001–0.0006) and temperature (from the range of 25°C–60°C) of the water-based NF contained GO NPs. It can be clearly seen that the conductivity significantly increases with mass fraction and decreases with temperature. Increasing the GO content noticeably intensifies the temperature dependence of conductivity.

The electrical properties of hybrid NFs are strictly dependent on the nanofiller's electric profiles. The study [42] relates to the TiB_2/B_4C NFs based on propylene glycol. It shows that the electric conductivity of B_4C NF is at least (the ratio increases when the NF temperature increases) about 70 times higher than the BF and about 63 times higher than mixed TiB_2 and B_4C NF. Such a situation can be associated with the differences in the conductivities and NP sizes of TiB_2 and B_4C, as it was also founded in EG-based SiO_2/Al_2O_3 hybrid NFs [43].

a)



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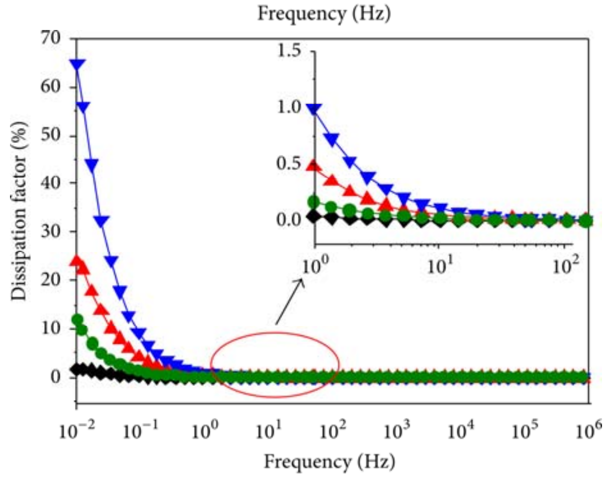

Fig.3. Frequency dependencies of: a) relative permittivity, and b) dissipation factor of vegetable oil modified by Fe_3O_4 NPs with different sizes: black – no filler, green – 8.6 nm, red – 15.2 nm, and blue – 24.4 nm [39]

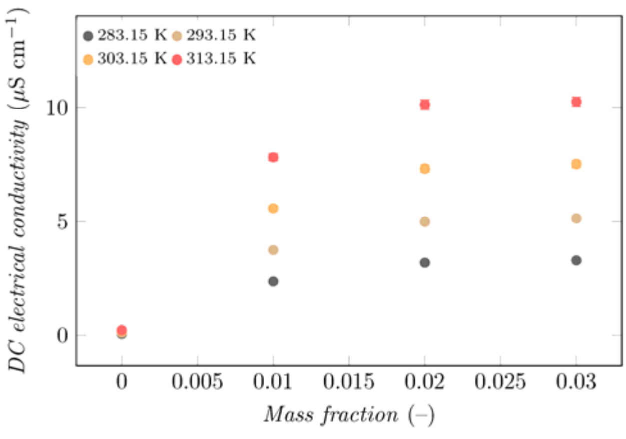

Fig.4. DC electrical conductivity as a function of nanofiller's mass fraction of the $CaCO_3$-EG NFs at various temperatures [40]

Factors that influence the electric conductivity of NFs are not only the types of nanofiller and BF, NPs mass fraction and size variations, but also sonication time during the production and surfactant/nanofiller mass ratio, as is shown in [17]. The paper presents the research on deionized water-base fluid mixed with the surfactant sodium dodecylbenzenesulfonate and doped with CNTs. From [17], it can be concluded that sonication time increases significantly (at least about twice) the conductivity, which is more visible when surfactant is added. However, the ratio of surfactant to filler begins to affect the conductivity (increase it) only after sonication is used.

Selected applications of NFs in electrical engineering

The vast majority of articles describing the use of nanofluids in electrical or power systems concern transformer technologies [44–46]. A lot of them relate to the improvement of transformer oil with the use of various metal oxides and graphene NPs. For example, a paper [44] reports the influence of the addition of TiO_2 (TO) and exfoliated hexagonal boron nitride (Eh-BN) NPs to the mineral oil (MO) as a base fluid on the AC breakdown voltage (ACBV), dielectric constant, and dielectric dissipation factor (DDF). It was found that nanofiller-contained oil demonstrates a way better ACBV (TO NF, approx. 46 kV, Eh-BN NF, approx. 75 kV) than pure MO (approx. 35 kV). The highest dielectric constant at 90°C was observed in Eh-BN NF, while the least was observed in pure MO. In the case of DDC, an inverse tendency was noted. The paper also describes the aging characteristics for the mentioned parameters: ACBV and dielectric constant decrease slightly while DDC slightly increases during the aging time.

Another study on the electrical and magnetic properties of the transformer with a liquid magnetic core made from Fe_3O_4 NF is presented in [45]. In the study, it was found that the inductance and coupling coefficient of coils increased while the concentration of Fe_3O_4 NPs increased. The use of ferro-nanofluid also causes an increase in the resistance of the transformer's coil and a decrease in its quality factor due to the phase delay between the magnetic field and the magnetization of the material.

The exploitation life of a transformer depends largely on the oil-impregnated paper's insulating characteristics. Chinese scientists examined the influence of insulating paper impregnation with oil containing different-size Fe_3O_4 NPs on the improvement in its dielectric properties. Schematically, the process of impregnation is shown in Fig. 5, while the details are described in [47].

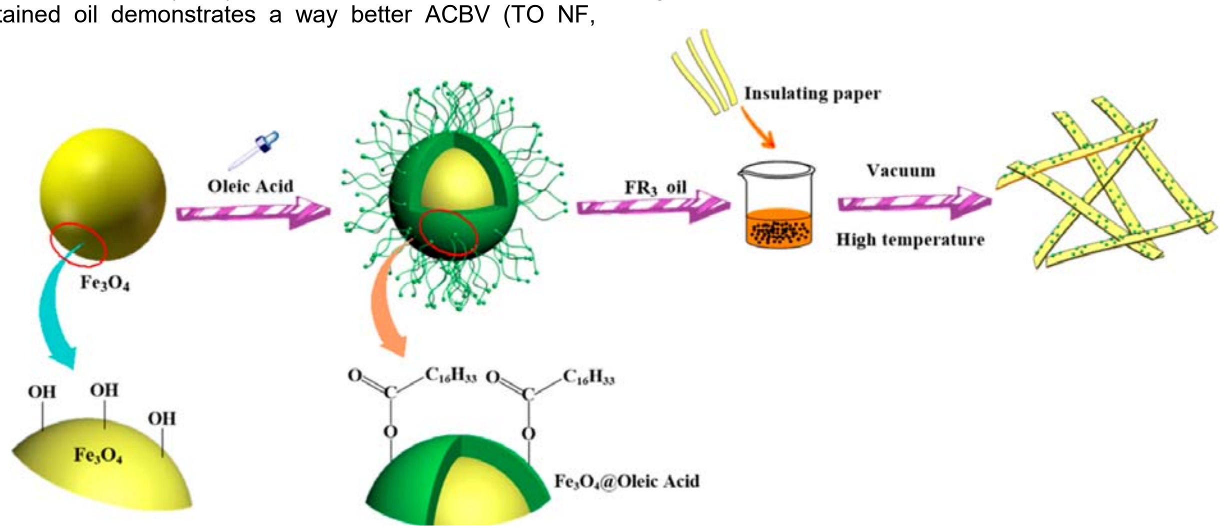

Fig.5. Preparation process of Fe_3O_4 NF impregnated paper [47]

Research showed that the maximum AC breakdown voltage of Fe_3O_4 NF-impregnated paper is 9.1% higher than that of pure oil-impregnated ones. The situation is similar in the case of DC breakdown voltage; its value increases by about 10.0% in comparison to just oil impregnation. Moreover, Fe_3O_4 NF impregnation increases significantly the relative permittivity of the paper (a bigger NP size corresponds to a higher permittivity). However, paper impregnation by NF with conductive NPs leads to an increase in electrical conductivity and dielectric loss afterwards, which should be taken into account when power equipment is designed.

NFs can also find applications in cooling systems for photovoltaic thermal (PVT) systems [48]. Egyptian scientists conducted research on traditional polycrystalline solar panels simultaneously under the same weather conditions for three experimental arrangements: the first module was a reference; the second was water-cooled; and the third module was cooled by a mixture of water and Al_2O_3 NPs (only 0.05% volume concentration), as shown in Fig. 6. They examined the electrical conversion efficiency in relation to the coolant used.

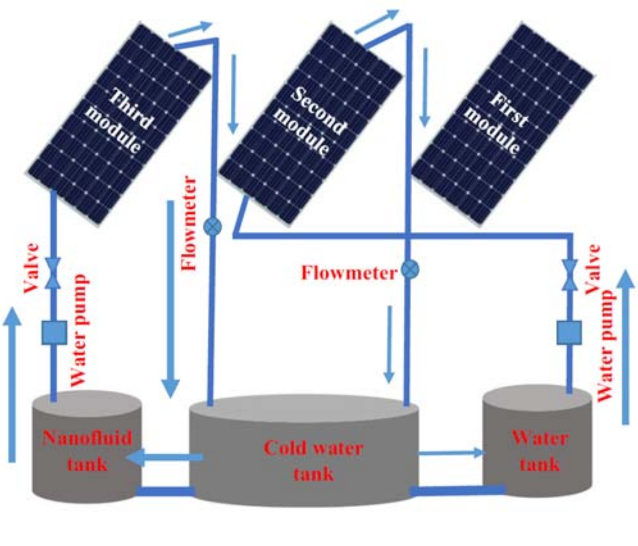

Fig.6. Schematic diagram of the PVT system [48]

It was discovered that the use of active Al_2O_3 NF cooling causes the biggest drop in PVT operating temperature (about 22.83%), which is crucial for the PV panel performance. This fact corresponds to the obtaining of the highest value of electrical efficiency of about 12.94% by the third module, while the efficiencies of the second and first modules are 12.53% and 11.99%, respectively.

NFs are beginning to be increasingly investigated for hydrogen production in the PVT panels through the electrolysis process [49–51]. During the electrolysis, the water splits into hydrogen and oxygen, while the first is separated and stored. Adding graphene or CNTs (i.e., carbon black with concentrations of 0.01 wt%~0.3 wt%) to water can significantly enhance hydrogen production, even up to 23.62% in comparison to pure water, as reported in [50]. The study [49] also shows an increase in hydrogen production when an electrolyte NF contains water, phase change material, and a small fraction of multiwalled CNTs (MWCNTs), ranging from 0.05 vol% to 0.15 vol%. The results showed that a maximum hydrogen production of 22% was noticed for a mixture with 0.10 vol% of MWCTNs.

Conclusions

Nanofluids containing metallic, metal oxide, graphene, and carbon nanotube nanomaterials demonstrate great application potential in not only heat transfer technologies but also in systems, the main issues of which are the insulating properties of electric or power devices, cooling systems for PV panel efficiency enhancement, PV energy conversion, energy and hydrogen storage systems, etc. If the key factors of the thermal properties of NFs, such as the alignment of magnetic NPs, NP size and shape, pH of the base fluid, surfactants, solvents, and hydrogen bonding, temperature, base fluid, and NP types, are studied at an advanced level, the influence of these parameters on their electric properties and dielectric performance needs more in-depth investigation. This will allow for the creation of more energy-efficient technologies for sustainable energy development as well as technologies that are friendly to the natural environment and ecology.

The grant was financed in the framework of the pro-quality program "Grants for grants" (Grant nr: 5/GnG/2022) of the Lublin University of Technology.

***Authors**:*
Oleksandr BOIKO: PhD Eng., assistant professor, Lublin University of Technology, Department of Electrical Engineering and Superconducting Technologies, 38A Nadbystrzycka St., 20-618 Lublin, Poland, E-mail: o.boiko@pollub.pl;
Radosław GAD: MSc Eng., senior lecturer, Lublin University of Technology, Department of Electrical Engineering and Superconducting Technologies, 38A Nadbystrzycka St., 20-618 Lublin, Poland, E-mail: r.gad@pollub.pl;
Makiko KOBAYASHI: Professor, Kumamoto University, Faculty of Advanced Science and Technology, Kurokami 2-39-1, Kumamoto 860-8555, Japan, E-mail kobayashi@cs.kumamoto-u.ac.jp;
Fumiaki MITSUGI: Professor, Kumamoto University, Faculty of Advanced Science and Technology, Kurokami 2-39-1, Kumamoto 860-8555, Japan, E-mail: mitsugi@cs.kumamoto-u.ac.jp;
Illia DIAHOVCHENKO: Professor, Sumy State University, Electric Power Engineering Department, 2 Rymskogo-Korsakova St., Sumy, 40007, Ukraine, E-mail: i.diahovchenko@etech.sumdu.edu.ua

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