

SEEBECK EFFECT IN COMPLEX FLUIDS & MAGENTA PROJECT (MAGNETIC NANOPARTICLE BASED LIQUID ENERGY MATERIALS FOR THERMOELECTRIC APPLICATIONS)

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SUNTO. – Materiali termoelettrici (TE) capaci di convertire calore in elettricità sono stati presi in considerazione come possibile soluzione allo scopo di recuperare calore di scarto a bassa resa (da processi industriali, motori, elettrodomestici o calore corporeo). Moduli termoelettrici (TE) basati su semiconduttori solidi sono stati i primi ad entrare in commercio e dominano tuttora il mercato TE. Malgrado la loro robustezza tecnica che include una lunga durata di vita e una semplicità di utilizzo per mancanza di parti mobili, la tecnologia TE è rimasta limitata ad applicazioni di bassa potenza a causa della scarsa efficienza. Dopo la nascita e crescita della nanotecnologia negli anni 1980-1990 si è assistito, negli ultimi 20 anni, ad un aumento vertiginoso della ricerca nel campo dei materiali termoelettrici che ha condotto a notevoli miglioramenti nella capacità di conversione di energia termica in energia elettrica. Ciò malgrado che anche i materiali più “promettenti” non abbiano ancora raggiunto gli standard ZT minimi richiesti. Inoltre, i materiali TE allo stato solido soffrono di una serie di inconvenienti pratici quali le piccole dimensioni, gli alti costi di produzione e l'utilizzo di materia prima scarsa e/o tossica che ne preclude l'utilizzo su larga scala. E' chiaro pertanto che è necessario un balzo in avanti nella ricerca di materiali TE che sia in grado di rendere la tecnologia termoelettrica ecologicamente compatibile ed economicamente accessibile per il futuro impiego. MAGENTA è un progetto di ricerca & innovazione della durata di 4 anni che punta ad un rovesciamento paradigmatico nella tecnologia TE basato sullo sfruttamento delle proprietà magneto-termoelettriche (MTE) di ferrofluidi (FF) basati su liquidi ionici (IL) e dispersioni colloidali costituite da nanoparticelle magnetiche (MNP) in liquidi ionici non magnetici. Le nanoparticelle magnetiche sono, come il nome stesso suggerisce, una classe di nano particelle (meno di 1 micron di diametro) contenenti elementi magnetici quali ferro e nickel e loro leghe e composti chimici. Queste sono già in uso in una pletera di campi della tecnologia che va dalla biomedicina all'immagazzinamento di dati nei computer. Tuttavia il loro uso in campo energetico rimane per ora

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molto limitato. Viceversa i liquidi ionici (IL) stanno ricevendo una crescente attenzione negli ultimi anni nella ricerca in campo energetico che include la termoelettricità. Come materiale termoelettrico i liquidi ionici presentano una serie di caratteristiche interessanti che vanno dalla elevata conducibilità elettrica ad ampie finestre di temperatura e potenziale elettrochimico, bassa tensione di vapore parziale e tossicità e abbondanza di materia prima. In questa presentazione discuterò le motivazioni scientifiche di MAGENTA (è come cioè generare potenziali termoelettrici e correnti usando ferrofluidi in liquidi ionici) e discuterò inoltre le metodologie da utilizzare e gli obiettivi del progetto che consistono in: 1) fornire la conoscenza di nuovi fenomeni magneto-termoelettrici che si manifestano in ferro fluidi basati su IL; 2) costruire prototipi MTP disegnati con IL-FF's con specifica applicazione per l'utilizzo in settori industriali (automobili e strumentazione elettronica portatile). Presenterò infine alcuni incoraggianti risultati preliminari ottenuti dai collaboratori del progetto sui materiali liquidi termoelettrici.

ABSTRACT. – Thermoelectric (TE) materials that are capable of converting heat into electricity have been considered as one possible solution to recover the low-grade waste-heat (from industrial waste-stream, motor engines, household electronic appliances or body-heat). Solid semiconductor-based TE-modules were the first to enter the commercial application, and they still dominate the TE-market today. Despite their technical robustness including long life-time, simple use involving no moving parts, TE-technology has long been limited to low-power applications due to their poor efficiency. Closely following the rise of 'nanotechnology' in the 1980's - 90's, there has been a huge increase in the TE materials research in the past 20 years, which has led to some remarkable improvements in thermal-to-electric energy conversion capacity. However, even the most "promising" materials have not yet reached the minimum ZT requirements. Furthermore, solid TE-materials suffer from a variety of practical obstacles such as small sizes, substantial production costs and the use of scarce and/or toxic raw materials, precluding them from wide-scale applications. Clearly, a technological breakthrough in TE-materials research is needed in order to make the thermoelectric technology environmentally friendly and economically viable for its future use. MAGENTA is a 4-year research & innovation project that aims at bringing a paradigm change in TE-technology by exploiting the magneto-thermoelectric (MTE) property of ionic-liquid (IL) based ferrofluids (FF), *i.e.*, colloidal dispersions consisting of magnetic nanoparticles (MNPs) in non-magnetic ionic liquids. Magnetic nanoparticles are, as the name suggests, a class of nanoparticles (less than 1 μm in diameter) made of magnetic elements such as iron and nickel and their alloys and chemical compounds. They are used in a plethora of technological fields from biomedicine to data storage. However, their use in energy applications remains quite limited so far. Ionic liquids (IL), on the other hand, are enjoying substantial attention in several areas of energy research including thermoelectricity in recent decades. As a thermoelectric material, ILs present many promising features such as high electrical conductivity, large temperature and electrochemical windows, low vapour pressure and toxicity, and raw material abundance. In this presentation, I will discuss MAGENTA's *scientific motivations* (how to produce thermoelectric voltage and current using IL based ferrofluids), *the methodologies* to be used and *the project objectives*; *i.e.*, 1) to provide founding knowledge of novel MTE phenomena in IL based ferrofluids, and 2) to build application-specific MTE prototypes with tailor-made IL-FFs for their use

in targeted industrial sectors (cars and portable electronics). Some encouraging preliminary results on liquid thermoelectric materials obtained by the project partners will also be presented.

1. INTRODUCTION

Today, heavy reliance on fossil fuels over renewable energy sources continues, witnessed by the acceleration of world's primary energy consumption growth in the past 30 years (reaching 13000 MToe (million tons oil equivalent) in 2014). Meanwhile, much of the consumed energy is wasted in the form of heat at all levels of human activity. For example, thermal loss amounts to as much as 20-50% of total energy consumption across different industrial sectors (1) and as much as 60-70% in internal combustion engine vehicles (<http://energy.gov/eere/vehicles/vehicle-technologies-office-waste-heat-recovery>). Therefore, if even a small fraction of 'waste-heat' can be converted into more useful forms of energy such as electricity, it should lead to considerable energy savings.

Thermoelectric (TE) materials that are capable of converting heat into electricity have been long considered as a possible solution to recover the low-grade waste-heat from industrial waste-stream, motor engines, household electronic appliances or body-heat. Solid semiconductor-based TE-modules were the first to enter the commercial application, and they still dominate the TE-market today. Despite their technical robustness including long life-time, simple usage involving no moving parts, TE-technology has long been limited to low-power applications due to their poor efficiency; which is most often expressed in terms of a dimensionless parameter, "figure of merit" ZT . ZT combines materials' three transport coefficients; namely, the electrical conductivity σ , the thermal conductivity κ , and the Seebeck (thermoelectric) coefficient S_e , and the average temperature T of the system (2), *i.e.*, $ZT=(\sigma S_e^2/\kappa)T$. For TE-devices to be competitive against other renewable energy technology (*e.g.*, geothermal), ZT values greater than 4 are considered mandatory (3). Closely following the rise of 'nanotechnology' in the 1980's - 90's, there has been a huge increase in the TE materials research for the past 20 years. Nanostructuring of TE materials essentially aims at lowering the lattice heat conduction while enhancing the Seebeck coefficient, which has led to remarkable improvements in thermal-to-electric energy conversion capacity. However, even the most

“promising” materials have not yet reached the minimum ZT requirements, and it is unlikely that $ZT > 3$ can ever be achieved through nanostructuring of solid materials. Furthermore, solid TE-materials suffer from operational, environmental and economic issues such as their small sizes, substantial production costs and the use of scarce and/or toxic raw materials. Clearly, a technological breakthrough in TE-materials research is needed in order to make the thermoelectric technology environmentally friendly and economically viable for its future use.

One possibility is found in liquid-electrolytes whose observed TE-coefficients are generally at least one order of magnitude larger than the semiconductor counterparts, including nanostructured materials. The electrical conductivity of these liquids, however, is a few orders of magnitude lower than solid counterparts and therefore, liquid based TE-systems have long been considered technologically irrelevant despite their advantages; *e.g.*, material abundance, low production costs, *etc.*. Recent advances in the in ionic liquids and ionic-liquids/solvent binary mixtures, however, is giving renewed hope in the development of liquid thermoelectrics. Ionic liquids (IL) are molten salts that are liquid at room temperature and up to high (decomposition) temperatures extending above 200-400°C. ILs’ possess large electrical conductivity values compared to other liquid electrolytes and some have wide electrochemical windows (4) making them suitable for variety of low-grade waste heat recovery applications. The thermoelectric modules containing such liquids are often referred to as “thermoelectrochemical cells” or simply “thermocells,” depending on different TE-effects used to induce the desired thermoelectric energy conversion; *i.e.*, thermogalvanic, thermodiffusion and/or temperature dependent electronic double layer formation effects. Today, the most widely studied TE-effect in ionic liquids is that of thermogalvanic effects; *i.e.*, temperature dependent electrochemical reactions between the redox-couple molecules and the electrodes. (5).

Another type of fluids recently being explored are charged colloids, also known as ionic nanofluids. In energy applications, nanofluids have been widely considered as cooling agents for their superior thermal transfer properties. Their ability to convert heat into electricity, on the other hand, is only recently been reported. From theoretical point of view, the thermo(electric)-diffusion of charged colloidal particles and macromolecules in liquid electrolytes are thought to make non-

negligible contribution to the fluid's Seebeck coefficient due to their large sizes (6). Indeed, in nanofluids where charged nanoparticles are known to possess very high thermodiffusion coefficient (Soret coefficient), a direct link between the transport entropy of the particles and the resulting Seebeck coefficient has been reported (7).

In the following sections, brief and salient descriptions of three most dominant physical origins of thermoelectric potential production in complex liquids are given.¹ Then recent experimental evidences on the combined thermodiffusion and the thermoelectrochemical effects in magnetic nanofluids (ferrofluids) are recounted as an example. Our current understanding of thermo-electro-chemical nature of complex fluids is far from complete, encouraging further experimental and theoretical research and development efforts in this exciting field of liquid thermoelectrics.

2. THERMOELECTRIC (SEEBECK) PHENOMENA IN THERMOCELLS

In a typical thermocell, (an example given in the *Fig. 1*) TE-liquid is in direct contact with two electrodes. When a temperature gradient is applied different across the cell, several thermoelectric phenomena take place. The temperature dependent electrode potential is generated which is often referred to as "Seebeck potential", although the physical and electrochemical mechanisms behind such phenomena in liquids are quite different from the Seebeck effect in solids. There are predominantly three different effects that induce Seebeck potential in liquid thermocells; thermogalvanic effect of redox species, thermodiffusion of ionic species and the formation of electronic double layer at electrode/liquid interfaces.

2.1 Thermogalvanic cells

Today, the thermoelectric applications of liquid electrolytes are predominantly focused on thermogalvanic cells in which a redox cou-

¹ Note that in-depth introduction on the physics and electrochemistry of these phenomena are beyond the scope of the current article, but references to useful articles and books are given for interested readers.

ple is dissolved in the electrolyte. The redox reaction between two species of A and B involving n -electrons is described in Equation 1.



The electrons in the redox reaction are either given to or taken from the electrodes, thus generating electrical current that can be extracted to be used as a power source. Under such condition, the thermocells functions as a thermoelectric generator (TEG).

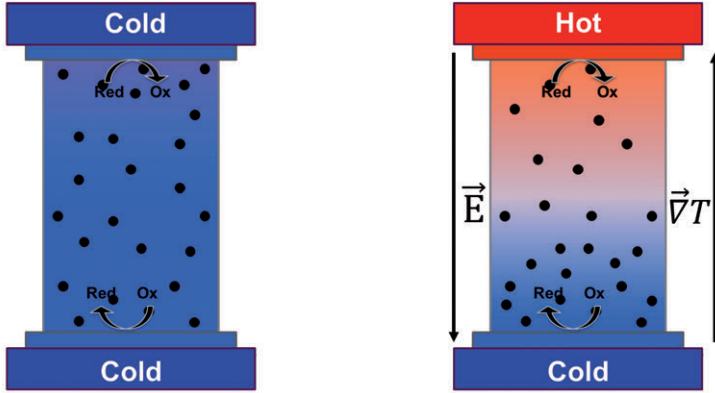


Fig. 1. Schematic view of a typical thermocells in isothermal condition (left) and under a thermal gradient ∇T (right). Upon the application of ∇T , thermodiffusion of ionic species, thermogalvanic reaction of redox species and the formation of electronic double layers occur, all of them contribution to the overall Seebeck potential across the thermocell.

The redox reaction potential depends on temperature and thus a thermoelectric potential ∇V is produced between the hot and cold electrodes of a thermocells;

$$\Delta V = \frac{\Delta S_{AB}}{nF} \Delta T = S_{e_{TG}} \cdot \Delta T \quad (2),$$

where ∇S_{AB} is the partial molar entropy change of the redox reaction, n is the number of electrons transferred in the reaction and F is the Faraday constant. ΔS_{AB} is known to depend not only on the redox species, but also on the ionic strength of the surrounding electrolytes and the electrode materials. The most well-known example of thermocells is, perhaps, that of aqueous potassium ferro/ferricyanide redox solutions, presenting Seebeck coefficient values ($S_{e_{TG}}$, subscript TG for

thermoelectric) in the order 1 mV/K (8). Recently, Dupont *et al.*, have published a review article on thermo-electrochemical cells in which compiles the state of the art progress of thermoelectric effects (Seebeck potential and power generation) observed using a variety of ionic liquids, redox couples, electrode materials and their combinations (5). The highest (published) Seebeck coefficient is found with cobalt-based redox couple, larger than 2mV/K over a wide temperature range extending well above 100°C.

2.2 *Electronic double layer (and other phenomena at electrode-liquid interface)*

A thermocells can also function without the presence of redox species; but in this case no electrical current flows in and out of the cell, thus it operates as a thermally chargeable capacitor (TCS). The thermoelectric potential is then produced primarily by the temperature dependent surface potential at the liquid/electrode interfaces. On the electrode surface, ions lose a part of their solvation layers and their entropy is modified. The electrical energy is then stored in the form of charge accumulation at the electrode interfaces, which can be subsequently recovered by 'discharging' through an external load.

The Seebeck coefficient observed in TCS's ($S_{e,C}$, subscript C for capacitor) are generally higher than EGs mentioned above. For example, Se as high as 7mV/K was observed in non-aqueous electrolytes (9) and 4 mV/K in ionic conductors (10). In ionic liquids, there has been a tremendous surge in the numerical simulation and experimental efforts to understand how electronic double layer formation and the capacitive behaviors of IL-electrochemical cells; *i.e.*, iso-thermal electrochemical cells are charged electrically. These results can be extended to thermal charging of electrochemical cells. (11) (12) (13). Furthermore, change in ionic concentration at the electrode/liquid interface can greatly influence the electrochemical reaction potential of redox species (see previous section), therefore can modify the overall Seebeck coefficient even in thermoelectric cells (14).

2.3 *Thermoelectric effect*

The thermoelectric potential production in complex liquids is further coupled to the movement of dissolved charged species (ions, mol-

ecules or colloidal particles). It is closely related to the thermodiffusion effect, or also known as “Soret effect,” which describes the concentration (n) gradient induced under a temperature gradient;

$$\frac{\nabla n}{n} = \alpha \nabla T \quad (3).$$

The Soret effect in complex fluids such as nanofluids has been extensively studied in the past (see for example (15) (16) (17)) and is often used as a part of microfluidic characterization and separation techniques. The Soret coefficient, α , is generally proportional to the entropy transported by the moving molecules or particles (*i.e.*, internal degrees of freedom, large solvation shell, particle/molecule size, etc.). Therefore, large thermoelectric coefficients can be expected in complex liquids exhibiting large values of α . In simplest terms, the Soret coefficient (α) of colloidal particles and the thermoelectric-diffusion term in the initial Seebeck coefficient (S_{e-D} , subscript D for diffusion) of the fluid are linked to one another through a physical quantity known as Eastman entropy of transfer, \hat{S} , via;

$$\alpha = (\hat{S} - \xi e S_e^{st}) / k_B T \quad (4)$$

$$S_{e-D}^{ini} = \sum_i \frac{t_i \hat{S}_i}{\xi_i e} \quad (5),$$

In equation (4) ξ is the effective charge of the moving particle, e the electron charge and S_e^{st} , the stationary Seebeck coefficient of the fluid (see (7) and its SI documents for more explanation). In Equation (5), the subscript ‘ i ’ indicates that the diffusion term of the Seebeck coefficient S_{e-D}^{ini} is the sum of contributions from all charged species (electrolytes, redox couples, charged nanoparticles, etc.). t_i , ξ_i and \hat{S}_i denote the Hittorf number, effective charge and the Eastman entropy of transfer of i_{th} charge specie, respectively. In the context of colloidal solutions, the Eastman entropy of transfer describes the interaction between the particle surface and its surrounding liquids. It needs to be emphasized here, that while the Soret coefficient describes the thermally induced concentration gradient (Equation 3) at the “equilibrium state;” *i.e.*, *after* all motions of particles cease, while the Seebeck coefficient (S_{e-D}^{ini}) here corresponds to that of “initial state;” *i.e.*, *before* the thermally induced motions take place. The latter may

be interpreted that the thermoelectric potential created by the $S_{e,D}^{\text{ini}}$ effect is a partial source of electromotive force used for diffusing the colloidal particles. The first experimental observation directly linking the two coefficients ($S_{e,D}$ and α) through the Eastman entropy of transfer was reported in ferrofluids, which will be discussed in the following section.

Note that $S_{e,D}^{\text{ini}}$ exists for redox species and electrolyte ions although their contributions to the overall Seebeck coefficient tend to be much smaller compared to the thermogalvanic one and thus are generally ignored. However, the Eastman entropy of transfer of large electrolyte molecules does appear to influence the overall Seebeck coefficient and can be detected experimentally in the case of slow mass transfer of redox species and electrolyte ions. (18) (19)

3. THERMOELECTRIC AND THERMOELECTRIC DIFFUSION EFFECTS IN FERROFLUIDS

The influence of internal electric field on the thermodiffusion of charged colloidal particles became an active area of research in the last decade and the theoretical models were used to explain experimental observations in various colloidal ionic fluids (See for example (20) (21) (6)). Curiously, the thermoelectric potential counterpart in the same process remained unexplored. The first of its kind measurement was reported by Huang *et al.*, on ionic ferrofluids where a quantitative agreement was found on the Eastman entropy of transfer values determined independently from thermodiffusion (Soret coefficient) and thermoelectric (initial Seebeck coefficient) measurements (7). In the second study presented here, the effect of ionic strength on the initial Seebeck coefficient in ferrofluids was explored. The findings here set a possible course for future theoretical and experimental research in the field of thermoelectric phenomena in complex fluids. (22)

3.1 *Eastman entropy of transfer: The link between the thermodiffusion (Soret) and initial thermoelectric (Seebeck) coefficients*

In this study published in 2015, the Soret, α , and the initial Seebeck, S_e^{ini} coefficients were investigated in a ferrofluid consisting of

charge-stabilized maghemite nanoparticles dispersed in organic solvent (dimethyl sulfoxide). Both coefficients were measured as a function of magnetic nanoparticles concentration (ϕ). Note that the ferrofluids also contained small amounts of redox couple (ferrocene and ferrocenium). The thermodiffusion of nanoparticles was measured using Forced Rayleigh scattering technique, while the thermoelectric field is accessed through TE-voltage measurements in a thermocells (7). The $\alpha(\phi)$ and $S_e^{\text{ini}}(\phi)$ values were fitted using the theoretical model to estimate nanoparticle's Eastman entropy of transfer (\hat{S}_e) independently as shown in Fig. 2.

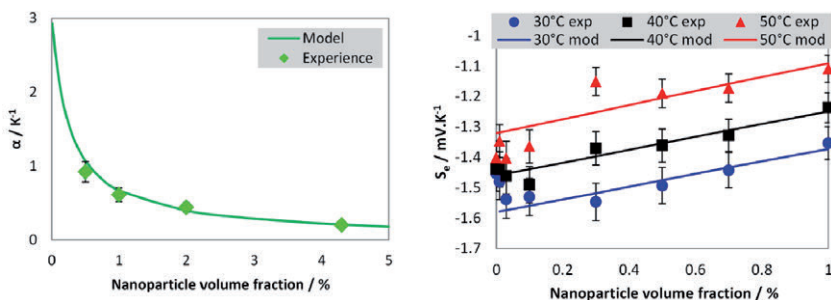


Fig. 2. (Left) Soret coefficient α as a function of NP concentration (vol%) measured at $T=23^\circ\text{C}$. (Right) Initial Seebeck coefficient measured at 30, 40 and 50°C as a function of NP concentration (vol%). The S_e values at 0% concentration corresponds to the thermogalvanic term (see Section 2.1). Solid lines are the fitting results using Equations 4 and 5 (from Section 2.3) from which the Eastman entropy of transfer values were extracted (7).

The value of the Eastman entropy of transfer from the Soret and Seebeck coefficient measurements are quite large, $\sim 75 \text{ meV.K}^{-1}$, which is a few orders of magnitude larger than those found in small electrolyte ions. This observation effectively demonstrated that the thermodiffusion of charged nanoparticles with a large Eastman entropy of transfer can influence both the thermodiffusive and thermoelectric properties of colloidal solutions.

3.2 The effect of ionic environment on the initial seebeck coefficient of aqueous ferrofluids

In this second example, aqueous ferrofluids containing ionically

stabilized colloidal magnetic nanoparticles using different counter-ion types were studied. More specifically, two aqueous ferrofluids made with identical magnetic nanoparticles that are ionically stabilized with either TBuA^+ or Li^+ counterions. These ferrofluids had previously been measured for their thermodiffusion properties which revealed that the counterions control the magnitude and the sign of the nonparticles Soret coefficients are altered from a large and positive (thermophobic) value for TBuA -coated NPs to a smaller and negative (thermophilic) value for Li coated ones. (23) The NP concentration dependence of the initial Seebeck coefficient in ferrofluids was found to be quite different from one type of counterion to another as seen in *Fig. 3* below.

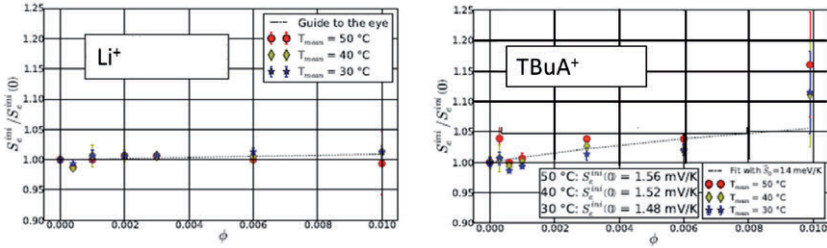


Fig. 3. Normalized initial state Seebeck coefficient as a function of the NP volume fraction (ϕ) with Li^+ (left) and TBuA^+ (right) counterions. ∇T of 10K were used for all measurements. Note that ferro/ferricyanide redox couple was added to the solution whose known thermogalvanic coefficient $\sim 1.5\text{mV/K}$ corresponds well to the S_e values obtained without nanoparticles ($S_e(0)$) at different temperatures (22).

In the case of ferrofluids with TBuA^+ as counterions, the initial Seebeck coefficient is found to increase as much as 15% for NP volume fraction of 1%. On the other hand, with Li^+ as counterions, no appreciable change was detected. These observations were explained in terms of 1) large Eastman entropy of transfer, \hat{S} , of both NPs (14 meV/K) and TBuA^+ and 2) large effective charges, ξ (~ 300), of NPs inferred from the electrical conductivity measurements in the ferrofluids with TBuA^+ counter ions (not shown here). The study demonstrates that both \hat{S} and ξ of nanoparticles are sensitive to its ionic environment; *i.e.*, counterion choice, and that with a proper control of such parameters, one can indeed increase the thermoelectric power of liquid thermocells.

4. FUTURE RESEARCH DIRECTION: MAGENTA PROJECT

The thermoelectric voltage and current production in complex fluids relies on complex functionalities of different constituents (electrolytes, nanoparticles, redox couples, etc.) and the interactions between them. The underlying mechanisms that govern the stability and the observed TE phenomena in these liquid materials are only starting to be understood. Thus, theoretical/mathematical modelling and simulations of constituents and their multi-scale interactions; from molecular orbital interactions to collective thermodiffusion of particles and the formation of electronic double layers at the liquid/electrode interface, will become crucial for building foundational knowledge for the proposed magneto-thermoelectric materials research in liquids.

From the application point of view, the experimental findings presented above suggest a new technological path to improve the energy conversion capability of liquid thermoelectric materials using charged colloidal particles. Within the existing theoretical framework, the observed increase can be attributed to the large value of Eastman entropy of transfer in conjunction with a large effective surface charge of colloidal particles (in initial Seebeck coefficient). Moreover, the application of magnetic field is known to increase the Soret coefficients of ferrofluids, further encouraging the use of ferrofluids for magneto-thermoelectric energy conversion applications.

In this context, the project MAGENTA² intends to take advantage of magnetic nanoparticles' unique and tuneable properties (magnetic and thermoelectric) combined with the ionic liquid's thermoelectric properties and their wide working temperature range to develop novel magneto-thermoelectric devices using ionic liquid based ferrofluids (IL-FFs). Both experimental and theoretical approaches are employed to build foundational knowledge on novel magneto-thermoelectric phenomena in IL-FFs. Simultaneously, the project aims to build application-specific magneto-thermoelectric prototypes with tailor-made IL-FFs for their use in targeted industrial sectors (interested readers are invited to visit the project website <https://www.magenta-h2020.eu>).

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