AAPG2022	TTIMSCAP	JCJC
Coordinated by:	Jérémie MAIRE	48 months
Axe H.8 : Sciences de base pour l'énergie (CE 50)		

Thermo-tomography of buried Interfaces in Micro-Supercapacitors

I. Pre-proposal's context, positioning and objective(s)

Context

Thermal transfers are completely transversal among technological applications and span all temporal and spatial scales. The most widespread example of the issues that can arise from heat might be the thermal management in mobile devices, with thermal throttling commonplace in mobile phones and laptops. To devise efficient thermal management solutions for devices comprising micro- and nano-components, the literature is full of works aiming at elucidating the mechanisms governing heat transfer at these scales.

Current technology developments for a smart society rely heavily on autonomous devices and sensors with multiple components integrated on-chip. Alongside energy generation, storage is a critical element of such devices and batteries, with their high energy densities and low self-discharge rates, are currently the main storage solution. Supercapacitors present a promising alternative for applications requiring higher charge/discharge rates and better cyclability (up to 1000x that of Li-ion batteries) or as a hybrid solution when coupled to a battery. The performances and characteristics of these devices are strongly impacted by external temperatures but also from heat dissipation during the charge/discharge cycles, especially via the Joule effect. Indeed, the electrical and thermal performances of a supercapacitor are closely linked. [1] However, whereas supercapacitors and on-chip micro-supercapacitors (MSCs) are widely studied, including for flexible electronics applications, few studies focus on their thermal properties. To date, thermal or electro-thermal models are mostly used to interpret the behavior of the devices. Alongside the development of predictive models, local and global thermal properties now need to be measured.

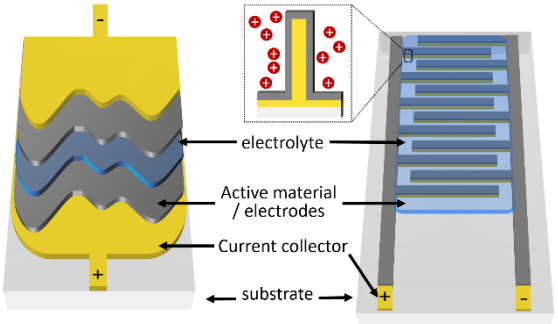

Figure 1 Schematics of on-chip MSCs in out-of-plane (left) and in-plane interdigitated (right) configurations. The in-plane MSC can have increased surface via a forest of nanostructures.

Therefore, it is necessary to develop a technique catered to multiscale and heterogeneous devices. Indeed, MSCs comprise nanoscale or hierarchical materials and patterned areas –e.g., electrodes and current collectors– in millimetric devices, thus spanning 4 to 6 orders or magnitude in size. The characteristic times for charge/discharge are typically on the order of seconds or lower, with some dynamics as fast as a few microseconds. Further, MSCs are made of many materials, including an electrolyte that can be a solid, gel or liquid. Thermal investigations in MSCs thus need to account for multiphysical phenomena, including conduction, radiation and potentially convection at multiple spatio-temporal scales.

Measuring global thermal parameters for a whole device is thus not sufficient, but micro and nanoscale thermal properties remain challenging to measure even for individual materials. Developments are ongoing in scanning thermal microscopy, particle-based techniques in fluids or optical methods such as thermoreflectance. Regardless of the heat transfer scales, detection systems compromise either in terms of field-of-view or spatial or temporal resolution. The balance between these aspects is particularly problematic as physical phenomena in heat transfer get faster as dimensions decrease. Indeed, hot carriers can be created and relax to heat the lattice in a matter of picoseconds. Although these timescales seem far from many technological applications, thermal management become increasingly challenging is smaller components functioning at continuously increasing frequencies. This challenge further increases with component integration moving towards increasingly complex 3D technologies with processing, communication and power delivery elements combined in a single device. The combined timescales and dimensions required to measure temperatures in such devices require optical techniques, despite the wavelength-dependent limit set by diffraction. In the visible spectrum, temperature measurements are often limited to surface measurements. Indeed, the thermoreflectance technique usually requires a metallic transducer and can access the thermal conductivity λ of one buried thin film alongside that of the substrate, or a superlattice,

together with the contact resistances. A phonon spectrometer spanning a record-broad spectrum of frequencies was recently developed based on thermoreflectance techniques. Combining such spectrometer with local probe techniques solves the issue of the diffraction limit, but is extremely heavy to implement and impractical for multiscale characterization. Infrared cameras on the other hand can access information in the depth of materials, as many common materials such as silicon are semi-transparent in the mid-IR range, but the resolution suffers from the increased wavelength. Inversion methods are furthermore instrumental in retrieving the properties of the materials and eventually reconstructing heat sources within devices. [2,3]

Objectives

The goal of the project is to retrieve the time-dependent temperature field T(x,y,z,t) within MSCs in-operando and reconstruct internal heat sources and heat propagation in the devices. These measurements will yield the thermal diffusivities within the materials but also give information of the contact resistances that are often the bottleneck in heat dissipation. This information will contribute to design more efficient MSCs and later be applied to other devices. Practically, the project objectives can be divided in two main categories.

The first goal will be to develop an experimental system capable of reconstructing the 3D time-dependent temperature field in a heterogeneous microstructure using contactless optical techniques. This setup, combined with real-time analysis and post-processing, needs to output not only the temperature field T(x,y,z,t), but also thermal diffusivities. From these values and complementary measurements, we will be able to extract thermal conductivities and specific heat of the materials, as well as all the interface resistances.

The second goal will be to apply this new technique to the complete thermal characterization of MSCs in operation. From the measurements, we will retrieve the temporal thermal behavior of the different materials, including T(x,y,z,t) and the thermal properties as detailed above. We will then provide thermal design guidelines based on the data obtained with different MSC designs, especially thermal interface resistances.

Methodology

The advancement of the project will rely on a combination of my expertise in optical systems and nanoscale heat transfer, and the team in I2M who has a strong expertise in experimental heat transfer characterization (IR thermo-spectroscopy, tomography, photothermal measurements [4] and the flying spot technique [5] to cite the main ones) with numerical inverse methods that have been successfully used for super-resolution imaging and reconstructing embedded 3D heat sources. [2]

The challenge of bridging a broad range of temporal and spatial scales is complexified by the heterogeneity of the materials and the interfaces between materials, components and even devices. Interfacial thermal properties become critical in complex nanostructure assemblies, which can contain different materials, geometries, sizes. They can limit thermal dissipation and even change the properties of a material when it lies on a substrate, e.g. graphene on substrate as opposed to suspended graphene.

To overcome these challenges, we will develop a confocal time-resolved thermo-transmittance system to access temperature information within the devices. A supercontinuum laser accordable in wavelength from visible to the mid-IR will be used to avoid the issue of the opacity of solid materials. The broad range of wavelengths has two additional advantages. First it can be adjusted to fit the optical properties of many materials, providing versatility to the system. Second, it enables confocal spectroscopic measurements, which will provide additional information about the local chemistry of the materials, such as the electrolyte. Combined with confocal microscopy, this will enable the 3D mapping of the thermophysical properties of the device. For non-operating devices and isolated materials, a second laser will serve as a pump to heat the sample. Fast acquisition of multiscale temporal dynamics will rely on a heterodyne scheme,

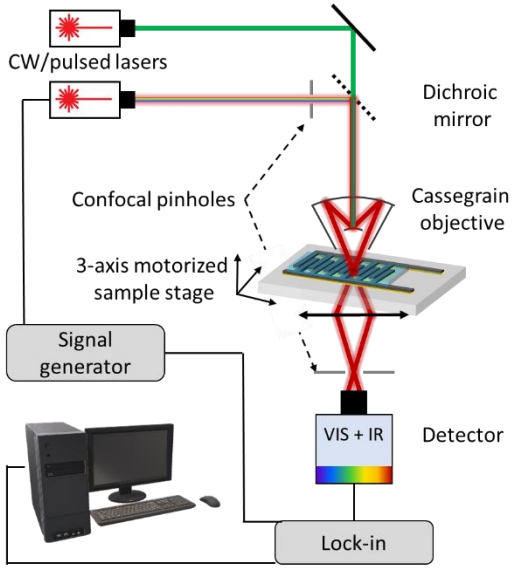

Figure 2 Schematic of the experimental setup. The supercontinuum laser is used as the probe to perform transmittance and spectroscopic measurements. The pinhole represents the confocal part of the system and the acquisition can be performed with a lock-in amplifier and a heterodyne scheme for the fast timescales.

that is the pulsed probe laser will be synchronized to the periodic heating with a slightly shifted repetition rate. The repeated acquisition over many cycles enables the reconstruction of the temporal trace. This technique is not necessary for the slowest dynamics in the system, which can be acquired directly with fast photodetectors. This setup can be further enhanced thanks to its modularity. Indeed, a natural evolution will be the implementation of a Raman spectrometer that can be used in parallel as a thermometer via confocal optothermal Raman measurements, as well as to obtain chemical/composition information.
The data that will be obtained from the measurement, namely the temperature field, will then be post-processed. The first point is to improve the resolution beyond the diffraction limit. This will be done by combining displacements of the samples with steps of 100 nm, with an algorithm that has been recently developed in the team. Obtaining the thermal properties of the materials and reconstructing the spatio-temporal profile of the heat sources will be done with inversion methods, which also constitute one of the core know-hows of the host team. The quadrupole method, among other analytical and numerical models, will be applied to 3D temperature fields to extract thermal interface resistances.

Innovative nature of the project

The project innovates through two main aspects, namely the development of the experimental platform and the characterization of in-operando MSCs.
The first part constitutes the first implementation of a 4D (spatio-temporal) system giving thermal information at the microscale and below and adapted to systems containing solid materials. From a physical knowledge perspective, the 3D transient temperature field will give information of thermal transfer at interfaces within the device, as surface techniques such as time or frequency-domain thermoreflectance are limited to one or two layers below the transducer depending on the number of free parameters in the model. The novel technique will complement existing characterization principles such as IR spectroscopy and make use of measurements procedure such as the flying spot technique, all of which are available in the team with IR cameras in the 4-6 um and 7-13 µm ranges. The know-how in the team combined with my experience in laser microscopy and fast phenomena will provide comprehensive thermal characterization for embedded energy systems and microelectronic devices.
The second part, dedicated to the understanding of heat transfer in complex devices will start with validating the method in simple structures, but rapidly address the thermal challenges in MSCs during charge-discharge cycles and later on during their operation in fully integrated devices.
The breakthroughs expected in the project will also be critical in other research areas such as biology and medical treatments based on nanoparticle heating, where thermal properties and heating are at the core of the techniques. The applications are therefore numerous and potentially related to several scientific fields, which contributes to the innovative nature of the project.

Budget

The total budget requested for this project is 294 k€. The main costs are divided between the salary for a PhD candidate (122.5 k€) and the cost for building the setup, namely equipment, including the laser and a set of two detectors to cover the ranges of wavelength of the laser (81 k€), and parts and consumables (37 k€). The remaining expense are related to environmental cost like a computer for image processing, services, mobility and open access publications, as well as overheads.

Ability of the project to address the research issue covered by the CE50

Heat is involved in many of the energy transformation, harvesting or production processes. The TTIMSCAP project aims at developing a new experimental technique to measure temperature as well as thermal interface resistances and thermal diffusivities of in-operando energy devices, the study case for the project being micro-supercapacitors. This characterization technique combines a multiscale spatial and temporal approach with numerical inversion methods and a super-resolution algorithm. As such, the project clearly answers to themes and research challenges developed in the CE50, especially the advanced characterization for energy processes section. Indeed, the project will yield an experimental method and innovative instrument for complex systems, at multiple spatial and temporal scales and with Multiphysics considerations. Furthermore, the multiscale characterization will be performed in-operando. The system proposed in this project can further enable multiphysics measurements linked to energy processes in a broad range of devices and is modulable.

II. Partnership (consortium or team)

Since the start of my PhD, defended in 12/2015, I have developed and used several non-contact optical systems for thermal and structural characterization of micro and nanomaterials. [6–8] This went on throughout my PhD and first postdoc (University of Tokyo, 2012-2016), and my second postdoc in the Catalan Institute of Nanoscience and Nanotechnology (ICN2, Spain, 2017-2020). Measuring the thermal properties of micro and nanostructures made of graphene, which is incidentally a material often used in MSCs, remained the focus of my following position as a Marie-Curie fellow initiated in Institut NEEL in Grenoble in 2020. In most of my papers (which number 26), I have made use of characterization systems based on optical techniques that I have developed or contributed to developing to investigate the thermal properties of micro and nanostructures. **One year ago, I joined Thermal Imaging Fields and Characterization (TIFC) team at I2M** as a Chargé de Recherche (CR) CNRS for a trial period of one year (the full nomination, effective November 2021, was recently approved). The TIFC team specializes in thermal characterization via IR imaging techniques and photothermal systems, as well as inverse methods, the combination of which is applied to both solids and microfluidic devices for heat and mass transfer.

The TTIMSCAP project clearly emerges from a synergy between my expertise and competences and those of the TIFC team. The project will also reinforce the developing collaboration with the LIMMS in Tokyo, where I conducted my PhD research. Energy is one of their main research axes, with a strong ongoing activity about energy harvesting for autonomous sensors such as thermoelectricity, flexoelectricity, and flexible applications. A natural collaboration emerges with the new system proposed in TTIMSCAP. I plan to spend several weeks in LIMMS to develop this collaboration. This project will bring me and the TIFC teams strongly towards embedded energy systems.

My integration in the TIFC is currently ongoing via three different channels: (i) Jean-Luc Battaglia, Professor, who will be the PhD director for the student asked in this project, (ii) collaborations on numerical methods such as super-resolution with M-M. Groz, CR CNRS, and (iii) S. Chevalier, Associate Professor (MCF) ENSAM, who has involved me in a PhD thesis he is currently co-supervising on IR transmittance measurements with a camera. From January 2022 I will be the coordinator of a Nouvelle-Aquitaine regional project that has been accepted in the 2021 call and recently started. Building on this, this JCJC project will bolster my own research activity to develop a specific research line on energy systems and through it my leadership skills. Furthermore, M-M. Groz and E. Abisset-Chavanne (Professor and TIFC member) will bring expertise in numerical methods and contribute to the inversion, heat source reconstruction and super-resolution challenges of the project.

Finally, this **JCJC project can be seen as the first important step towards a double objective of a thermal tomography system and bridging length and temporal scales in thermal characterization**. Among the numerous challenges, multiphysical characterization need to be addressed to move from isolated measurements to comprehensive analysis. This evolution of the current JCJC proposal will be developed in a future ERC Consolidator proposal that will build upon the activity initiated here.

III. References related to the project

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