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On the photothermal characterization of liquid thermoelectrics. New methodology based on coupled pyroelectric-Seebeck effects, together with frequency and thickness scanning procedures

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ABSTRACT

A new, combined photopyroelectric-photothermoelectric (PPE-PTE) technique, coupled with both thickness (TWRC) and chopping frequency (FS) scanning procedures, is proposed for thermal characterization of liquid thermoelectrics (LTE). The PPE-TWRC technique, in back detection configuration was used for the direct measurement of the LTE's thermal diffusivity. Based on the results obtained for thermal diffusivity, two PPE-FS scans, performed at two different thicknesses are used for the precise determination of absolute LTE's thicknesses. Simultaneously, PTE-FS scans, performed at the same thicknesses, lead to the value of LTE's thermal effusivity. The main advantage of the proposed technique, compared with previously reported procedures based on the TWRC scan, is a more precise determination of absolute LTE's thickness. In such a way the possible influence of the slow Soret effect is eliminated. The results, obtained on octanol + 0.1 mol l^{-1} TDAN (tetradodecylammonium nitrate), $\alpha = 6.77 \times 10^{-8}$ m^2s^{-1}, e = 602 $Ws^{½}$ m^{-2} s^{-1}, k = 0.15 W m^1 K^{-1}, are in good agreement with previously reported data.

1. Introduction

During last decades contact photothermal (PT) techniques have been largely used for thermal characterization of various condensed matter materials [1]. Among them, the photopyroelectric (PPE) and the photothermoelectric (PTE) techniques, proved to be suitable especially when characterizing liquid samples, due to the fact that the thermal contact between a solid (sensor) and a liquid (sample) is perfect and consequently, accurate results are expected.

In such a PPE/PTE calorimetry, a sample is irradiated with an optical beam, and the heat, generated in the sample due to the absorption of radiation, is measured with either a pyroelectric or thermoelectric sensor which is in good thermal contact with the sample [2,3]. The physical mechanisms for these two techniques are different (pyroelectric and Seebeck effect, respectively), but the final result is, in both cases, a current generation due to a thermal gradient. Various detection configurations (back or front), sources of information (amplitude and/or phase of the signal), and scanning parameters (chopping frequency of radiation and/or thickness of one liquid layer) have been used, depending on the purpose of the investigation [4,5].

One application of this type of calorimetry is the thermal characterization of the thermoelectric materials. The thermoelectric (TE) generators are intensively studied in connection with their energetic applications. The efficiency of a TE device depends on material characteristics such as the Seebeck coefficient (S_0), thermal (k), and electrical (σ_0) conductivities, and the figure of merit $zT = TS^2\sigma_0/k$ is used to compare TE device performances.

Recently, Kuriakose et al. [3] proposed, for thermal characterization of solid TE generators, a front detection configuration based on a cell consisting of two layers: a directly irradiated TE generator and a liquid with known thermal properties. Using as scanning parameter the chopping frequency of laser radiation, the methodology allowed the determination of two dynamic thermal parameters (thermal effusivity, e, and diffusivity, a) of the material used as a sensor.

On the other hand, it is well-known that the thermoelectric effect occurs also in liquid electrolytes due to the presence of several ion species. The growing interest for liquid thermoelectrics (LTE) is connected to the fact that Seebeck coefficients up to 7 mV/K have been found [6]. Recently, Touati et al. proposed two methods for thermal characterization of LTE-s. One method is based on heating successively the front and back faces of a cell containing a TE liquid material [7]; by measuring the resulting Seebeck voltage between the electrodes and after an adequate signal processing, the thermal parameters can be found. The second method proposes a simultaneous PTE-PPE measure-

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ment coupled with the TWRC scanning procedure. PPE will lead to the direct and accurate measurement of LTE's thermal diffusivity and then, the value of thermal effusivity can be derived from PTE investigation [8].

In this paper we proposed for thermal characterization of liquid thermoelectrics a new, combined photopyroelectric-photothermoelectric (PPE-PTE) technique, coupled with both thickness (TWRC) and chopping frequency (FS) scanning procedures. The PPE-TWRC technique, in back detection configuration was used for direct measurement of the LTE's thermal diffusivity. Thermal diffusivity is then used in two PPE-FS scans, performed at two different thicknesses for the precise determination of absolute LTE's thicknesses. Simultaneously, PTE-FS scans performed at the same thicknesses lead to the value of LTE's thermal effusivity.

The proposed method is an alternative to the second method proposed by Touati, but with some advantages. In order to clarify these advantages we have to take into account the basic PTE phenomenon produced in LTEs. The PTE signal in LTEs is generated by an associated Soret-Seebeck effect. Soret effect consists in fact in mass diffusion (separation of ionic species due to a thermal gradient) and it can be sometimes slower than the heat conduction in the LTE. This fact depends on many experimental parameters as: nature of the electrolyte, chopping frequency of the incident radiation, detection time constants and speed of data acquisition, etc. This is why the saturation of the PTE signal, predicted by the theory for thick LTEs [8] is not always observed. In such cases, the method proposed in ref. [8] is not suitable anymore. However, as demonstrated in [8], the useful PTE information comes from the thermally thin up to "not too thick" regime of the LTE (thickness of the liquid smaller than 2–3 thermal diffusion lengths). Consequently, a methodology based on the data collected only in this thermal regime can eliminate the discrepancies observed at thick LTE's. Such a method is proposed in this paper. PPE-FS scans, performed at two different thicknesses are used for the precise determination of absolute LTE's thicknesses. A double check of the absolute LTE's thicknesses is performed by the indications of the micrometer used in the TWRC method. Consequently, the PTE information can be collected by using a normalized signal obtained in the thermally "not too thick" regime for LTE.

2. Theoretical aspects

The schematic of the detection cell is presented in Fig. 1.

The laser beam impinges on the opaque surface (in practice a thin metallic foil) of the LTE material. In Fig. 1 the front surface of the pyroelectric sensor ($LiTaO_3$) is located at the position $x = 0$, the thickness scan of the LTE material being performed along the positive direction of X-axis. l_1 and l_2 are two particular thicknesses of the liquid thermoelectric, selected for frequency scanning investigations.

2.1. PTE

Concerning the PTE detection, the configuration is "front" (the LTE material is the sensor − directly irradiated and situated in front position relative to the laser beam − and the pyroelectric material is the sample, situated in back position) and consequently, for weak temperature variations, the voltage signal generated by the LTE material is given by [5,7]:

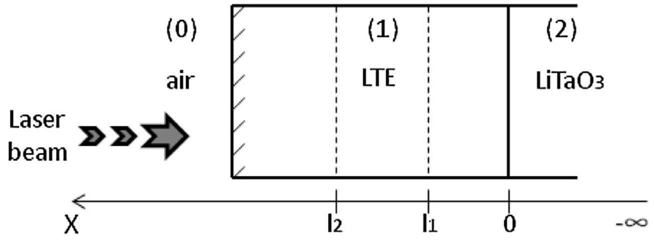

Fig. 1. Schematic drawing of the PPE-PTE detection cell.

$$\Delta\ V = [T(x = l) - T(x = 0)];\ \ l = l_1,\ \ l_2 \tag{1}$$

where S_0 represents the Seebeck coefficient and T is the temperature field across the detection cell.

If the opaque LTE is irradiated with a modulated laser beam of angular frequency $\omega = 2\pi f$ and only the fraction $(1\text{-}R)$ from its intensity H is absorbed by the thermoelement and transformed into heat, the temperature across the detection cell is given by the relationship [9]:

$$T(x) = S_0 \frac{(1 - R)H}{2k_1\sigma_1} \frac{\exp(-\sigma_1 l) + \gamma_{12}\exp[-\sigma_1(2l - x)]}{1 - \gamma_{12}\exp(-\sigma_1 2l)} \tag{2}$$

Inserting Eq. (2) in (1) we get:

$$\Delta V = S_0 \frac{(1 - R)H}{2k_1\sigma_1} \frac{1 + \gamma_{12}P^{-2} - (1 + \gamma_{12})P^{-1}}{1 - \gamma_{12}P^{-2}} \tag{3}$$

where

$$P = exp(\sigma_1 l);\ \ l = l_1,\ l_2;\ \gamma_{12} = \ (b_{12} - 1)/(b_{12} + 1);\ \ \sigma = (1 + \sqrt{-1})\left(\frac{\omega}{2\alpha}\right)^{1/2} \tag{4}$$

Eq. (3) indicates that, from theoretical point of view, if we perform a frequency scan of the PTE signal, at high enough chopping frequencies, or a thickness scan at enough large LTE thickness, the LTE becomes thermally very thick $(P = \infty)$ and, in principle, the PTE signal saturates. However, as mentioned in the Introduction, experimentally, this saturation was not always observed [7,8]. A possible explanation for such behaviour can be associated with the fact that, at high chopping frequencies the first opaque absorbing layer (considered in theory thermally thin) becomes non-negligible and influences the results. When using the TWRC scanning procedure, such an explanation is not valid anymore, because at constant chopping frequency the first irradiated layer is a constant heat source independent on its thickness. In this case the only possible explanation is that the Soret effect is too slow and, at large LTE thicknesses, the ion species are not completely separated, so no saturation of the PTE signal can be obtained. This is why in this paper we propose a more realistic alternative: to perform frequency scans at two different thicknesses l_1 and l_2, (thicknesses not too large − maximum 2–3 thermal diffusion lengths) and consider for analysis the normalized signal for the two thicknesses:

$$(\Delta V_n)_{1,2} = \frac{(1 + \gamma_{12}P_1^{-2} - (1 + \gamma_{12})P_1^{-1})(1 - \gamma_{12}P_2^{-2})}{(1 - \gamma_{12}P_1^{-2})(1 + \gamma_{12}P_2^{-2} - (1 + \gamma_{12})P_2^{-1})} \tag{5}$$

where $P_{1.2} = exp(\sigma_1 l_{1,2})$

Eq. (5) indicates that the electrical signal obtained from a LTE inserted in a sandwiched cell as presented in Fig. 1, and periodically illuminated with an optical radiation is a complex voltage which depends on its thermal diffusivity (α_1) and effusivity (e_1) and on the thermal effusivity (e_2) of the material situated in the backing position (the pyroelectric sensor). Knowing the pyroelectric's thermal effusivity, and LTE's thermal diffusivity (obtained as described in the next section) we obtain LTE's thermal effusivity (via Eq. (5)) by setting two different thicknesses, l_1 and l_2 and performing corresponding frequency scans.

2.2. PPE

Concerning the PPE detection, the configuration is "back" (the LTE is sample − directly irradiated − and the pyroelectric material is the sensor, situated in back position). In such a configuration for optically opaque sample and thermally thick sample and pyroelectric sensor, the phase of the PPE signal is given by the well-known relationship [10]: