



Thermal conductivity and temperature profiles in carbon electrodes for supercapacitors



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HIGHLIGHTS

- Comprehensive study of the thermal conductivity of carbon supercapacitor electrodes.
- Thermal conductivity for dry electrodes varied from 0.09 to 0.19 W K⁻¹ m⁻¹.
- Thermal conductivity for electrodes soaked in electrolyte ranged 0.30–0.48 W K⁻¹ m⁻¹.
- Modeling shows marginal temperature increase inside low ESR devices.

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ABSTRACT

The thermal conductivity of supercapacitor film electrodes composed of activated carbon (AC), AC with 15 mass% multi-walled carbon nanotubes (MWCNTs), AC with 15 mass% onion-like carbon (OLC), and only OLC, all mixed with polymer binder (polytetrafluoroethylene), has been measured. This was done for dry electrodes and after the electrodes have been saturated with an organic electrolyte (1 M tetraethylammonium–tetrafluoroborate in acetonitrile, TEA–BF₄). The thermal conductivity data was implemented in a simple model of generation and transport of heat in a cylindrical cell supercapacitor systems. Dry electrodes showed a thermal conductivity in the range of 0.09–0.19 W K⁻¹ m⁻¹ and the electrodes soaked with an organic electrolyte yielded values for the thermal conductivity between 0.42 and 0.47 W K⁻¹ m⁻¹. It was seen that the values related strongly to the porosity of the carbon electrode materials. Modeling of the internal temperature profiles of a supercapacitor under conditions corresponding to extreme cycling demonstrated that only a moderate temperature gradient of several degrees Celsius can be expected and which depends on the ohmic resistance of the cell as well as the wetting of the electrode materials.

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1. Introduction

Electric double-layer capacitors (EDLC), more commonly known as supercapacitors or ultracapacitors, are devices capable of fast and energy-efficient energy storage [1]. Unlike batteries, where electrochemical reactions or ion insertion is utilized to transform electric energy, supercapacitors store energy exclusively *via* electrosorption of ions onto the surface of highly porous carbon electrodes [1]. As a result, EDLCs exhibit intrinsically high power density and moderate energy density, whereas batteries exhibit the

opposite correlation; additionally, EDLCs show a long lifetime and up to 10⁶ charge/discharge cycles [2]. Commercial EDLCs commonly use organic electrolytes coupled with composite film electrodes composed of porous carbon (usually activated carbon; 85–95 mass %), polymer binder (5–10 mass%), and additives to improve the electrical conductivity (e.g., carbon black; ≈5 mass%) [3,4]. In the past decade, a large array of carbon nanostructures (e.g., carbon nanotubes, graphene, carbon onions), electrolytes (e.g., aqueous/organic solvents, ionic liquids), and functional electrode designs (e.g., thin films, printed electrodes, fiber mats) have been studied in detail with the goal of improving performance [5]. More specifically, many reviews have been published on electrode materials and electrolytes used in supercapacitors [3,5–8], best practice papers providing guidelines for electrochemical testing [4,9,10],

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studies on the degradation and aging of supercapacitors [11,12], and perspectives elucidating current trends and future potentials of this technology [13–15].

Compared to electrical conductivity, the thermal conductivity of EDLC electrode materials and thermal device properties have received less attention. The active component of film electrodes is carbon, and the thermal conductivity of graphite [16], graphene [17], carbon nanotubes [18], among other carbon materials, has been studied in great detail. From these studies, it is reasonable to assume a thermal conductivity in the range of 0.1–0.2 W m⁻¹ K⁻¹ for porous carbon, values reported for activated carbon measured in air [19]. These values are several orders of magnitude smaller than bulk carbon and graphite. Moreover, the thermal conductivity of porous materials can change significantly when adding liquids and applying compaction pressure. It is important to note that just a 10 K increase in temperature reduces the lifetime of an EDLC by a factor of two; therefore, a detailed knowledge of the thermal behavior of compressed porous electrodes with and without electrolytes is important when designing large scale EDLC systems [20].

For commercial applications it is common practice to model the thermal properties of a device in terms of the cell geometry. For instance, the temperature increase after one duty cycle of an EDLC device in a cylindrical cell can be described by a simple equation:

$$\Delta T = R_{\text{thermal}} I^2 R_{\text{el}} \quad (1)$$

where R_{thermal} is the thermal resistance, I as the current, and R_{el} as the dc resistance (or the high frequency resistance in the case of ac currents). In order to use this equation correctly, R_{thermal} must be defined in the equation to describe: the geometry, the heat capacity of the device, and the cycle. Consequently, Eq. (1) is then also only valid for one cycle and not at stationary state with many repeated cycles. This equation also only applies to the *external* temperature profiles of supercapacitors. In order to assess also the *internal* temperature gradients the thermal conductivities reported in this paper is required. The small temperature increases experienced by EDLCs can be attributed to the highly efficient, non-faradaic physical charge storage mechanism. To assess the thermal behavior of an EDLC device, Virtanen et al. [21], monitored the temperature of the air used to cool a 64 F supercapacitor module. They measured an increase of 15 °C when the device was operated up to 300 W. For comparison, lithium ion batteries, [22] may exhibit a significant temperature increase that require elaborate thermal management solutions to ameliorate safety concerns due to destabilizing battery modules [23]. A more detailed temperature profile study was carried out by Gualous et al. [24] for a 316 F supercapacitor cell under constant 20 W power in-/output cycling, they reported the external temperature increased first by approximately 6 °C and then remained constant at around 34–35 °C with very small thermal fluctuations inside the supercapacitor ($\Delta T < 1$ °C). The same trend was also found at higher power and for 60 W a temperature increase of almost 60 °C was observed. This study illustrates that not only the operating voltage but the cycling conditions play an important role in the thermal behavior of the device, especially when considering that the flash point for acetonitrile (82 °C) is very close to the observed temperature of the cycled device.

In this study, we investigate the thermal conductivity of film electrodes, composed of carbon and polymer binder, with and without electrolyte. In particular, we investigate to what extent the thermal properties of nanoscale carbon particles differs from micrometer-sized particles when processed into film electrodes, and how the electrolyte immersion affects the thermal properties. In addition to activated carbon, we have chosen carbon onions and multi-walled carbon nanotubes, which can be used as electrically conductive additives [25]. In addition to studying the thermal

conductivity, we also provide model calculations on the thermal behavior of full cells in different geometries. The aim of this paper is to provide data that can ensure more detailed and more precise thermal engineering of supercapacitors.

2. Materials and measurements

2.1. Thermal conductivity measurements

2.1.1. Apparatus

The apparatus used in the experiments is the same as the one reported in previous publications [26,27] and is depicted in Fig. 1. In brief, we measure the heat passing through a sample and the temperature difference across the sample. This gives us the thermal resistance of the investigated sample, R_{sample} . The sample can be a stack of materials or a single layer. Here, we measure the sum of the sample- and the contact thermal resistance, $R_{\text{sample}} + 2R_{\text{contact}}$. We also measure the sample thickness, which by Fourier's first law allows us to obtain the thermal conductivity.

A heat flux is set up in two cylindrical pistons (sandwiching the investigated sample) by flowing water with fixed temperatures in the upper and lower part of the apparatus. This heat flux is measured in each part of the apparatus by three thermocouples (1–3 and 6–8 in Fig. 1). Via calibration (see Ref. [26]) we know the thermal conductivity of the stainless steel and, by Eqs. (2) and (3), the heat flux through the sample (accuracy $\approx 97\%$). A small aluminum cap with thermocouples is placed close to the end of the two pistons (4 and 5 in Fig. 1). Because of the high thermal conductivity aluminum, these caps are close to isothermal and, thus, act like extensions of the thermocouples. Therefore we can measure the temperature drop across the investigated sample and the quality of the contact to the piston. By using calibrated micrometer gauges, we measured the thickness with a precision of ± 3 μm .

$$q_{\text{upper}} = k_{\text{steel}} \frac{T_1 - T_3}{\delta_{1-3}} \quad \text{and} \quad q_{\text{lower}} = k_{\text{steel}} \frac{T_6 - T_8}{\delta_{6-8}} \quad (2)$$

$$q_{\text{sample}} = \frac{q_{\text{upper}} + q_{\text{lower}}}{2} \quad \text{and} \quad R_{\text{total}} = \frac{T_4 - T_5}{q_{\text{sample}}} \quad (3)$$

2.1.2. Thermal conductivity measurements

We chose both to stack the investigated material and to measure individual layers. We chose four combinations of cylindrical

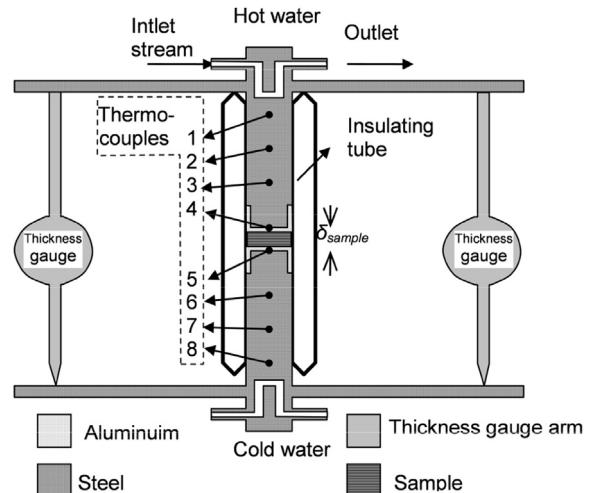


Fig. 1. A sketch of the thermal conductivity meter used for our study (cf. Ref. [26,27]).

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