

Chapter 2

Thermal Considerations for Supercapacitors

2.1 Thermal Management in Different Applications

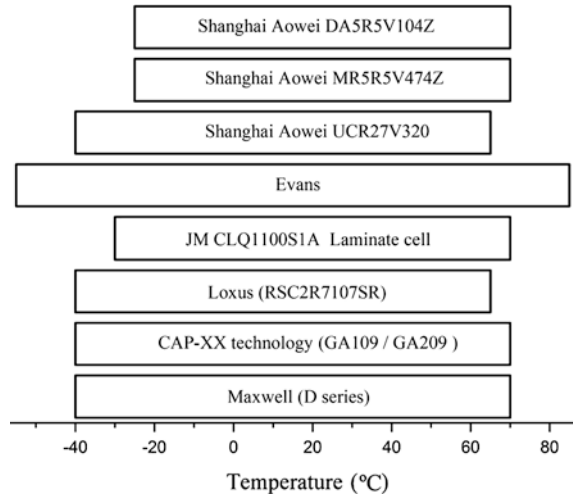
This section discusses thermal management of supercapacitors in different applications including the commercial supercapacitors used principally in hybrid vehicle transportation and electronic devices. Manufacturers typically prescribe safe operating temperatures of commercial supercapacitors in the range of -40 to 70 °C. Figure 2.1 summarizes the rated temperature range of various commercial supercapacitors. Thermal management of micro-supercapacitors and solid-state supercapacitors is also introduced in this section.

2.1.1 Commercial Supercapacitors

2.1.1.1 Supercapacitors in Heavy Electrical Applications

Supercapacitors typically possess a long-term life of millions of charge/discharge cycles and a low equivalent internal series resistance, allowing them to provide much higher power than battery packs of similar total energy ratings. Although ultracapacitor packs are relatively more expensive and store less energy per unit mass compared to batteries, they are expected to last the life of electric vehicles and are found to provide more fuel-efficient power in heavy electrical applications (e.g., automotive, hybrid transport). Combining supercapacitors with batteries can enhance performance in hybrid electric vehicles, including more powerful acceleration, braking energy recovery, outstanding cold-weather starting and increased overall system life. For instance, pulsed power during startups to reduce the duty cycle on a battery prolongs battery life, which can dramatically reduce battery replacement costs and improve reliability in vehicles. Because of their outstanding recharging capability and reasonable energy density, they provide applications such

Fig. 2.1 Temperature range of commercial supercapacitors



as automotive, heavy transportation, marine and traction with reliable engine starting over a wider temperature range than batteries.

Commercial supercapacitors have been successfully used in many applications such as electrical vehicles (EVs) and hybrid electric vehicles (HEVs) for capturing and storing energy from regenerative braking and supplying vehicle acceleration power. For instance, a supercapacitor are rapidly recharged at bus stops with charging stations to power EV buses in Shanghai, and supercapacitor modules are used as a power buffer in Honda fuel cell cars, which cannot respond to rapid changes in power in a few seconds [1].

The excellent low-temperature performance of supercapacitor modules makes them appealing to replace batteries as power supplies for cold cranking trucks in freezing weather, because batteries usually cannot provide enough power required to start the engine, whereas supercapacitors exhibit reliable performance even down to -40°C . Supercapacitors with excellent low temperature performance can easily satisfy the power needs in extreme weather conditions in heavy electrical applications. The automotive sector is now a steady source of revenue for supercapacitor manufacturers. Moreover, supercapacitors are also used in wind turbine pitch control, rail, and heavy industrial equipment.

2.1.1.2 Supercapacitors in Other Applications

Supercapacitors are also used in other applications such as electronics, grid balancing, and power backup by gradually protecting, enhancing, and replacing batteries in these applications. Incorporating supercapacitors into electronic or electrical equipment has usually resulted in improved performance, sometimes with lower lifetime costs.

Thinner, lighter, flexible or even transparent supercapacitors are needed for increasingly multifunctional consumer electronics. Reducing the thickness of the product designs has always been a priority in the mobile industry. One of the main constraints has been the dimensions of the power supplies. While the industry is currently reaching a plateau in terms of mobile thickness, the development of increasingly thinner and multifunctional power supplies seems to be exceptionally intriguing. Supercapacitors show promising advantages to satisfy the needs for consumer electronics, as compared to batteries, for the following reasons: (1) Pulsed loads that are common in portable battery-powered devices (e.g., mobile phones and other electronic systems) may cause temporary current spikes that exceed the steady state by many-fold, causing a large drop in battery voltage, which may lead to system shutdown. (2) In cold weather, batteries tend to be inefficient (degrading charge storage capacity) making them less capable of supplying loads than in warm weather. Because of the space restrictions in portable electronics, conventional electrolytic capacitors usually cannot support high current densities. On the other hand, supercapacitors with lower internal resistance, higher power and better low-temperature performance can solve the above issues. Supercapacitors used in these applications should be designed with lower upfront cost (expenses charged at the beginning of a project or business activity).

2.1.2 Micro-supercapacitors

The fast growing popularity of portable electronic devices requires continuous development and integration of micro-sized power sources to could meet demands in biological [2], medical [3] and environmental [4] applications. These micropower systems can be fabricated with smaller length scales (in a range of micrometers) and with better performance by decreasing ion diffusion lengths than their counterparts at macroscales. Typical micropower supplies include micro-batteries [5, 6], micro-supercapacitors [7, 8], and micro-fuel cells [9]. The power limitation remains a concern for Li-ion batteries, although nanomaterials [10], thin-films [11] or 3D structures [12] have been proposed to allow substantial improvements in the diffusion limitations of these redox-based systems. Supercapacitors storing energy by adsorption of ions from an electrolyte are a good alternative or supplement to batteries in high-power applications. The development of micro-supercapacitors on a chip with different electrode materials, structures, and electrolytes is thus an emerging field of research supported by the development of embedded micro-systems. A comprehensive review of micro-supercapacitors in terms of electrode materials, structural design and performance evaluation has been addressed in Ref. [13].

Apart from the requirements of high electrochemical performance, micro-supercapacitors also need to possess good thermal performance, since portable electronic devices are expected to work at different locations and temperatures. Additionally, in applications such as aeronautics and aerospace, electronic systems

undergo dramatic changes in temperature sometimes from the ambient at the earth surface to very low temperatures down to $-50\text{ }^{\circ}\text{C}$. Such extreme conditions require micro-power sources to be tolerant to large temperature fluctuations and function well. Like their macroscale counterparts, the temperature tolerance of micro-supercapacitors predominately depends on the electrolyte; therefore, a key to designing micro-supercapacitors with a wide operational temperature range is to design thermally robust electrochemical component elements, particularly electrolytes.

The prior published work has predominately focused on the electrochemical characterization of these micro-devices at room temperature, and relevant thermal characterization of micro-supercapacitors in a wide temperature range lacks systematic and thorough understanding. Until now, very few studies have reported the thermal behavior of micro-supercapacitors at different temperatures. Opportunities remain to enhance the thermal behavior of micro-supercapacitors by exploiting their unique properties such as adjustable gap distance, electrode thickness and current collector lengths and widths, shorter ion diffusion lengths and smaller electrode sizes.

2.1.3 Supercapacitors Based on Liquid- and Solid-State Electrolytes

The supercapacitor electrolytes can be classified into two main categories: liquid electrolytes and solid-state/polymer gel electrolytes. Liquid electrolytes include: (i) aqueous, (ii) organic and (iii) ionic liquid electrolytes. Most commercial supercapacitors available in market use liquid organic electrolytes because of their relatively high ionic conductivity (approximately 0.05 S cm^{-1}) [14], high voltage ($>2.7\text{ V}$) and good thermal stability over the rated temperature range (-40 to $70\text{ }^{\circ}\text{C}$). Recently, ionic liquids, which are room-temperature molten salts consisting mostly of organic ions, are attracting much attention because of their large liquid range (e.g., $[\text{C}_4\text{mim}][\text{NTf}_2]$: 89 to $450\text{ }^{\circ}\text{C}$), low vapor pressure and exceptional thermal stability at high temperatures [15]. However, hurdles such as high viscosity at low temperature and high cost are impeding the commercialization process of ionic liquid electrolytes. IL-based supercapacitors generally perform well at temperatures near or above $60\text{ }^{\circ}\text{C}$ [16]. The advantages of solid-state/polymer gel electrolytes over their liquid counterparts have been addressed in prior work [13]. The advantages of the solid-state/polymer gel electrolytes over their liquid counterparts include reduced leakage, improved safety and better packaging capability. Table 2.1 compares the general performance of supercapacitors based on liquid and solid-state polymer electrolytes.

Table 2.1 General comparison of supercapacitors based on liquid and solid-state polymer electrolytes [14–17]

| | Liquid electrolytes | | | Solid-state polymer electrolytes | | |
|---|----------------------|----------------------|--------------------------------------|--------------------------------------|----------------------------|------------------|
| | Aqueous electrolytes | Organic electrolytes | IL electrolytes | Water-containing | Organic solvent-containing | IL-containing |
| Upper voltage limit (V) | 1 | 2.7 | 1–4 | 1 | 2.7 | 1–4 |
| Ionic conductivity @ RT (S cm ⁻¹) | Up to 1 | 0.05 | 10 ⁻³ to 10 ⁻² | 10 ⁻³ to 10 ⁻¹ | 10 ⁻³ | 10 ⁻³ |
| Temperature range (°C) | –10 to less than 100 | –40 to 70 | RT to over 100 | –10 to less than 100 | –40 to 70 | RT to over 100 |
| Leakage problems | Y | Y | Y | N | N | N |

2.2 Thermophysical Properties of Supercapacitor Components

Thermophysical properties refer to the material properties that affect the transfer and storage of heat, and vary with many variables such as temperature, pressure and composition. Thermophysical properties of the components including thermal expansion, thermal conductivities and heat capacity of electrodes and separators, and viscosity, mass and diffusion coefficients of electrolytes are critically important to thermal transport in supercapacitor systems.

1. Thermal conductivity (W m⁻¹ K⁻¹): the heat flux through conduction is,

$$\dot{q}^{//} = -k \frac{dT}{dx}, \quad (2.1)$$

where $\dot{q}^{//}$ is the heat flux per unit time, k is the thermal conductivity, and $\frac{dT}{dx}$ is the temperature gradient along the x -direction. Higher thermal conductivity of the electrode material implies lower temperature rise for a particular heat flux. The thermal energy transfer process is random and involves diffusion through frequent collisions. Thus a mean free path of a thermal carrier between collisions is used to define the random nature of the thermal conductivity [18].

2. Heat capacity (J K⁻¹): the amount of heat energy required to raise the temperature of a body by 1°,

$$C_p = mc_p = \frac{\Delta q}{\Delta T}, \quad (2.2)$$

where ΔT is the differential temperature change due to differential heat absorbed Δq . The mass of the body and its specific heat capacity are given by m and c_p , respectively. Higher heat capacity implies more gradual temperature rise with time.

3. Thermal diffusivity α ($\text{m}^2 \text{s}^{-1}$): the ability of a material to conduct thermal energy relative to its ability to store thermal energy [18],

$$\alpha = \frac{k}{\rho c_p} \quad (2.3)$$

where V is density, and c_p is specific heat capacity at constant pressure.

4. Thermal expansion coefficient (K^{-1}): reflects the tendency of materials to undergo volumetric change in response to changes in temperature during a heat transfer process. Thermal expansion coefficient is defined as the strain of expansion divided by the change in temperature and generally varies with temperature. The volumetric coefficient of thermal expansion (α_V) for any gas, liquid, or solid, is,

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (2.4)$$

where V is the volume and the subscript p represents that the pressure during the expansion is held constant. Thermal expansion of supercapacitor components, particular the thin separators and thin polymer gel electrolytes films, is critically important to electrochemical performance and long-term stability of the devices during operation at elevated temperatures.

5. Viscosity ($\text{kg m}^{-1} \text{s}^{-1}$): The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress [19]. The viscosity of liquid electrolytes strongly affects the ionic conductivity in different temperature ranges. Thus viscosity (η) is a critical parameter to evaluate the efficiency of liquid electrolytes used in extreme temperatures and is defined as,

$$\eta = \frac{\tau}{\partial u / \partial y} \quad (2.5)$$

where τ is the local shear stress (N m^{-2}), and $\frac{\partial u}{\partial y}$ is the local gradient of the velocity along the y direction. The viscosity of an electrolyte is a function of several parameters, namely the type of anionic species, its size, relative capacity to form hydrogen bonds, van der Waals interactions and size of the cation [20].

6. Ionic conductivity (S m^{-1}): reflects the ion conduction rate through the liquid phase. The ionic conductivity of a set of ionic species is,

$$\sigma = \sum_i \mu_i n_i e_i \quad (2.6)$$

where σ , μ_i , n_i , and e_i are the ionic conductivity, mobility of ionic species i , concentration of carriers of species i and charge of species i , respectively. Ionic conductivity plays a pivotal role in determining the performance of supercapacitors. It is a function of the operating temperature and viscosity of the electrolyte. Ionic conductivity is often represented by the molar conductivity, Λ ($\text{S m}^2 \text{mol}^{-1}$). Ionic and molar conductivities are related by the following relation $\sigma = \Lambda c = \Lambda \frac{n}{V}$ where n is the number of the charge carrier in moles. The number of charge carriers present in volume V is $N = nN_A$, where N_A represents the Avogadro number.

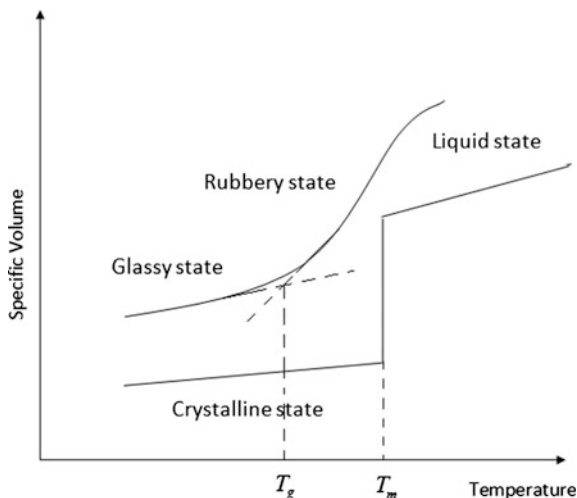
7. Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$): a proportionality constant between the molar flux and the gradient in concentration in a diffusive flow,

$$\dot{n} = D \frac{\partial c}{\partial x} \quad (2.7)$$

where \dot{n} is the molar flux of ions, and $\frac{\partial c}{\partial x}$ is the concentration gradient, which is inversely related to the viscosity of the electrolyte.

8. Melting temperature (T_m): the temperature at which the molecules or ions fall apart from their crystal structures and turn into disordered liquid. Polymer gel electrolytes exhibit both melting and glass transition temperatures because they consist of crystalline and non-crystalline (amorphous) phases in the solid state. Freezing point has the same meaning as melting point but in the opposite sense. Ionic liquids with some polymer electrolytes containing salts with long chains turn into liquid over a broad range of temperatures on heating. The lower limit for this change is called the melting point while the upper limit is called the clearing point. For ionic liquids, the melting and clearing points increase with increasing chain length. Room temperature ionic liquids (RTILs) exhibit melting temperatures below room temperature such that they stay in the liquid state and possess high ionic conductivity at normal operating conditions. Such ILs stay in the liquid state over a wide range of temperatures (as high as 300 °C) [21].
9. Glass transition temperature (T_g): the temperature of an object below which it behaves like a brittle material and above which it behaves as a rubber-like material. Generally, polymers consist of long chains and networks of linked atoms. They possess high viscosity in the liquid state. When they are rapidly cooled to temperatures below T_g , the molecular movement is too sluggish to take crystalline shape. Thus they stay in a non-equilibrium amorphous (non-crystalline) state which is termed the glassy state. The transition from liquid to glassy state is illustrated in Fig. 2.2. In general, the glass transition temperature is not a fixed number and is a function of the cooling rate. The glass transition temperature for ionic liquids can be tailored by selecting the proper combination of cations and anions [22]. In many studies, quantitative structure property (QSPR) models are used to estimate the glass transition temperature from the constituent ions of ionic liquids [23]. Ionic conductivity of the electrolytes

Fig. 2.2 Variation of specific volume with temperature for a polymer and a crystalline solid



increases drastically at temperatures above T_g but at the cost of decreased mechanical integrity. The influence of T_g on the thermal behavior of electrolytes is discussed in detail in Chap. 3.

10. Decomposition temperature: the temperature at which the polymer chains undergo breakdown due to chemical reactions. The decomposition temperature is expected to be lower in the presence of impurities such as oxygen in the polymer and higher in the presence of inhibitors and antioxidants. The temperature primarily determines the thermal stability of an electrolyte. It is experimentally determined by the weight loss obtained from thermal gravimetric analysis (TGA) measurements. Researchers generally ascribe 10–15 wt% loss to quantify the decomposition temperature. However, TGA results tend to overestimate long-term thermal stabilities [24]. Decomposition initially begins at temperatures far below this onset temperature [25–27]. Moreover, TGA samples are heated quickly and extremely briefly compared to long-term operation in real-world applications, resulting in an overestimation of the decomposition temperature. In order to understand the thermal decomposition of ionic liquid electrolytes better, more detailed information on decomposition mechanisms and kinetics is needed [28].

2.3 Mechanisms of Thermal Transport

Thermal transport describes the exchange of thermal energy between physical systems at different temperatures. The common modes of heat transfer are conduction, convection and radiation. Conduction, also known as heat diffusion, expresses the energy transfer between objects that are in physical contact. Thermal

conductivity reflects the ability of a material to conduct heat. The heat transfer in conduction process is given by Fourier's law of heat conduction (see Eq. (2.1)). Convection is the energy transfer between objects due to bulk fluid motion. The heat flux in convection process is,

$$\dot{q}'' = h(T_1 - T_2), \quad (2.8)$$

where T_1 and T_2 are the temperature of the two objects, and h is the heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$). Radiation is the energy transfer between objects at different temperatures by electromagnetic waves. The radiant energy transfer from body 1 at temperature T_1 to body 2 at temperature T_2 is expressed by the Stefan-Boltzmann law,

$$\dot{q}'' = \varepsilon\sigma(T_1^4 - T_2^4), \quad (2.9)$$

where ε is the emissivity of body 1, and σ is the Stefan Boltzmann constant.

Generally, in supercapacitors, heat is generated at the core during charge/discharge at high currents. This heat is carried away by conduction through the electrodes to the battery walls and finally dissipated by convection to the environment. The heat dissipation at the walls needs to be maximized to prevent the cells from overheating. The heat dissipation can be increased by maximizing the surface-to-volume ratio [29].

2.4 Experimental Techniques for Thermal Characterization

Many experimental techniques such as thermal gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and constant-current charge-discharge (C-D) have been utilized to characterize supercapacitor thermal performance and evaluate the thermal stability of supercapacitor components (electrode materials, separators, binder, and current collectors). This section briefly introduces such techniques and their application to thermal transport in supercapacitors.

1. Thermal gravimetric analysis (TGA): TGA is a method that has been commonly used to measure changes in physical and chemical properties of materials as a function of temperature with a constant heating rate or as a function of time with constant temperature and/or constant mass loss [30]. Information of physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption and chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction) can be revealed by TGA

results [30]. Selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture) can be determined from TGA data [30]. For application to thermal characterization in supercapacitor systems, TGA has proven an efficient method to evaluate the thermal stability of many supercapacitor components (e.g., electrode materials and electrolytes) [31–34].

2. Fourier transform infrared (FTIR) spectroscopy and time-of-flight (ToF) mass spectrometry: FTIR is usually used to obtain the wide-range infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas [35]. Part of the infrared radiation can be absorbed by samples and part of it can transmit, resulting in a spectrum that represents molecular absorption and transmission. Since no two unique molecular structures produce the same infrared spectrum, and the size of the peaks in the spectrum indicates the amount of material directly, FTIR can: (1) identify unknown materials; (2) determine the quality or consistency of a sample; and (3) determine the amount of components in a mixture. ToF mass spectrometry is a method that can determine an ion's mass-to-charge ratio by a time measurement [36]. These two techniques have been used to detect the decomposition compositions of electrolytes at extreme temperatures or during some abusive tests [37].
3. Differential scanning calorimetry (DSC): DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature [38]. DSC is a common thermal analysis technique that has been used in many applications such as analytical chemistry, process control and quality assurance. For instance, DSC analysis can shed light on the solid–liquid phase transition of RTILs.
4. Electrochemical impedance spectroscopy (EIS): EIS is an important technique to characterize electrochemical performance of supercapacitors. The x axis in the Nyquist plot obtained from EIS can be used to derive the equivalent series resistance R_s of a device, while the y axis can be used to derive the capacitance. The ESR and capacitance values are obtained using the following equations,

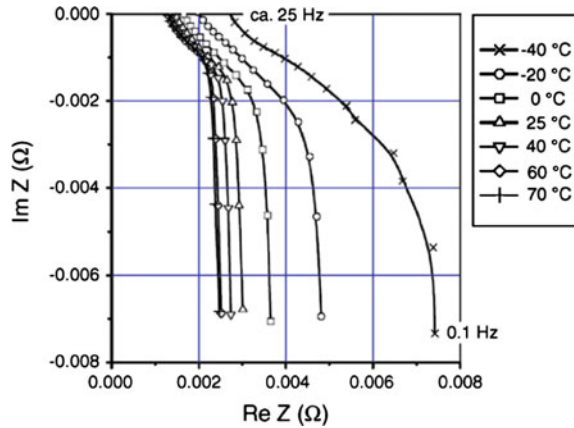
$$\begin{aligned} R_s &= Z', \\ C &= \frac{-1}{2\pi f Z''}, \end{aligned} \quad (2.10)$$

where Z' and Z'' are the real and imaginary parts of the impedance obtained at low frequencies, f , around 10 mHz. These equations are obtained by modeling the capacitor as a series RC circuit (see Fig. 2.3).



Fig. 2.3 RC series equivalent circuit for a supercapacitor

Fig. 2.4 Nyquist plots of impedance data for a BCAP00350 capacitor as a function of temperature, reprinted with permission from Ref. [39]. Copyright © 2005 Elsevier



Nyquist plots at different operating temperatures show the dependencies of capacitance, ESR and leakage resistance of the supercapacitor on temperature. Figure 2.4 provides a typical example of Nyquist plots for a BCAP00350 capacitor as a function of temperature [39]. From the figure, we can conclude that the ESR at $-40\text{ }^{\circ}\text{C}$ is much higher than that at $70\text{ }^{\circ}\text{C}$.

5. Cyclic voltammetry (CV): In a cyclic voltammetry experiment, the voltage of the working electrode is swept linearly with time, and the corresponding current is measured. The obtained current is plotted with the voltage applied which is called the CV curve. The specific capacitance C_s (F g^{-1}) is [13],

$$C_s = \frac{1}{2sm(V_h - V_l)} \oint_{V_l \rightarrow V_h \rightarrow V_l} I(V)dV, \quad (2.11)$$

where s represents the scan rate, V_h and V_l represent high and low potential limits of the CV curve, I is the instantaneous current, m is the mass of the active electrode materials, and V is the applied voltage. Rectangular-shaped CV curves are characteristic of pure double-layer capacitors, while peaks or humps are characteristic of pseudocapacitive behavior. The redox peaks are used to understand the change in electrode/electrolyte composition at elevated temperatures.

6. Constant-current charge/discharge: In these tests, supercapacitors are charged and discharged under constant current condition until they reach pre-set voltage limits. It is an efficient technique to characterize the electrochemical performance of supercapacitors (e.g., capacitance, internal resistance and cyclic life) [13]. The voltage variation is recorded, and the capacitance is,

$$C = \frac{I}{dV/dt} \quad (2.12)$$

where I is the applied constant current, and dV/dt represents the slope of the discharge profile after the initial voltage drop of the discharge curves.

2.5 Performance Evaluation Metrics

Various performance metrics (e.g., specific capacitance, long-term stability, and energy density) have been used to characterize supercapacitors in the literature. However, widespread agreement on what performance metrics and units to use is still elusive. The lack of standardized approaches in measuring and reporting results generates difficulties when comparing the performance of different devices [13]. For this reason, radar plots have been suggested to compare electrochemical performance of supercapacitors reported in different studies. Commonly used metrics to evaluate the thermal performance of supercapacitors are the operational temperature range, capacitances, energy and power densities at different current densities, equivalent series resistances, and attributes of different components of supercapacitors (e.g., ionic conductivities, viscosity and glass transition temperature of electrolytes, and thermal conductivity of electrodes). A radar plot is a useful method to summarize the thermal performance of supercapacitors and compare with other state-of-the-art results. Figure 2.5 provides an exemplary radar plot summarizing and comparing thermal performance of supercapacitors from two typical sources.

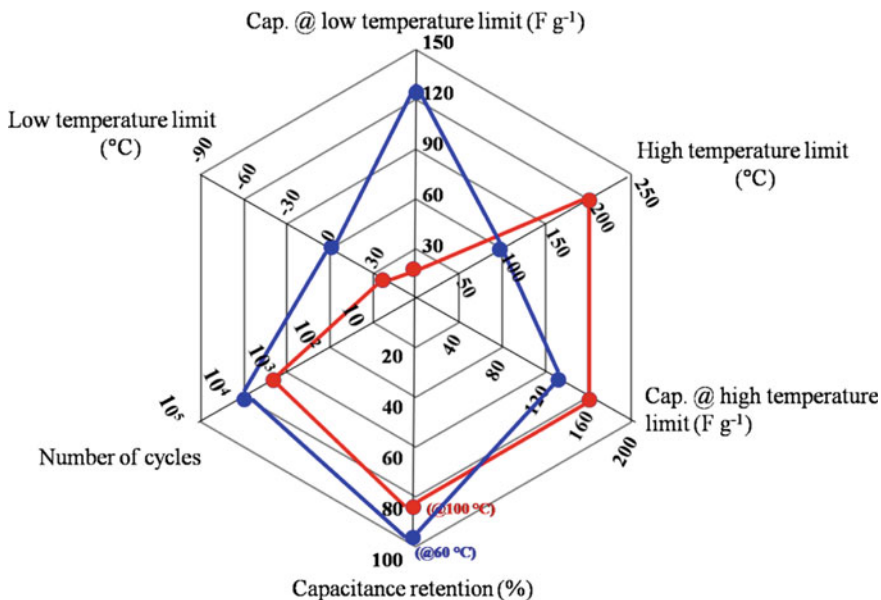


Fig. 2.5 Example radar plots to compare thermal performance two micro-supercapacitors cited from [40] (in blue) and [32] (in red). Blue and red curves are generated by connecting data points from supercapacitors based on pure ionic liquid electrolytes (BMPY TFSI) and BMIMCl-based ionogels polymer electrolyte, respectively. A missing data point in the radar plot indicates that the information about that category is unavailable in the reference

2.6 Supercapacitor Cooling Systems

Effective solutions to the issues associated with heat generation in supercapacitors often involve a thermal management system to maintain constant and lower temperatures. For instance, some thermal management systems are designed to maintain a supercapacitor pack at a set average temperature with uniform temperature distribution or only small temperature variations within the pack. This, however, adds additional volume and mass, as well as cost. It reduces the effective energy density of the system, and it may also reduce reliability, especially when pumps and fans are used to dissipate the generated heat. These provisions in turn necessitate the maintenance and servicing of the cooling systems, which is contrary to one of the most attractive features of supercapacitors—low maintenance [41]. Consequently, supercapacitors are equipped with a cooling system only when the maximum temperature exceeds approximately 65 °C [42].

Cooling systems are broadly classified into two types: active cooling and passive cooling. In active cooling systems, generated heat is carried away by an air flow through forced convection. Passive cooling systems often maintain temperature uniformity in the battery pack using a phase change material (PCM). The PCM matrix dissipates heat that is generated within the cells of a module by conduction. The advantage of such systems is that they require low to nil energy consumption. A schematic of a cooling duct for supercapacitor modules is presented in Fig. 2.6 [43]. The cooling system has a middle air inlet and two side outlets, which combine parallel and serial ventilation. By controlling the air flow rate, the maximum temperature in the capacitor bank can be controlled within a precision of 5 °C.

Commercial supercapacitor storage packs include multiple interconnected individual cells. For vehicle applications, the supercapacitor pack must be able to provide protection against unfavorable working environment such as vibration, shock, temperature, and corrosion from water, dust, and debris. Each supercapacitor cell contains an exterior casing and a pair of terminals. The supercapacitor packs need to be cooled, and their terminals and the copper interconnects between

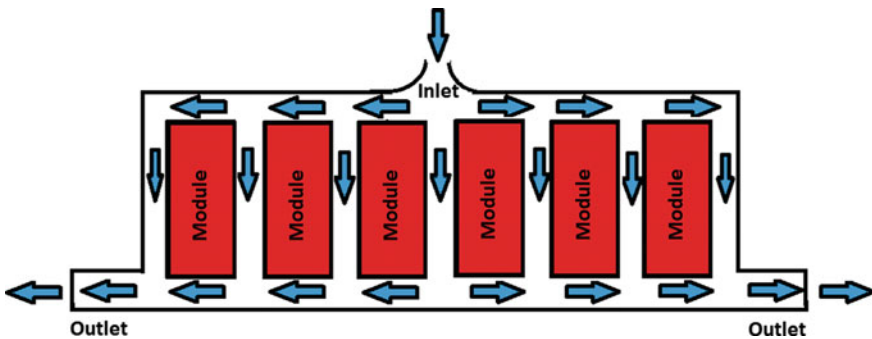


Fig. 2.6 Schematic of cooling systems (cooling air ducts) of a supercapacitor package, adapted from Ref. [43]

individual cells also need protection. The problem with previous cooling techniques for supercapacitors is that most mounting arrangements held the capacitors by the exterior casing, obstructing an important part of the supercapacitors for efficient cooling. A proposed way to cool the supercapacitors is to use cutout holes in the bottom plate to allow cooling air to circulate through the pack [44]. The individual cells used in supercapacitor packs are usually constructed in the form of cylinder with terminals placed on each end of the cell, in which case the majority of heat generated during the charge/discharge process is transferred to the environment through the two ends of the cell.

Blowing air across the cylindrical bodies/cases of the cells can efficiently cool the cylindrical cells. However, many new techniques have been adopted for more effective cooling. In a particular invention, a cooling system does not need air to be blown across the bodies of the cells [45]. The cells radiate heat in the axial direction upwards and downwards, and a blower and cooling assembly circulate a heat transfer fluid past the upper and lower respective terminal heat sinks outside the enclosure to cool the cells. Another invention [46] uses a two-phase system that pumps a cooling fluid through a closed loop. A modification of this invention [47] uses a spring plate to press the cold plates against the capacitors. The spring plate is able to flex, to allow the cold plates to be positioned to engage objects of different heights. The tube's serpentine shape also allows flexure, for positioning of the cold plates. An alternate or complement to a cooling system is to use a temperature sensor that decreases the charging current upon detection of an over-temperature condition [48].

Typically, the cooling system is larger for battery banks compared to supercapacitors [49]. A well-designed thermal management system should ensure good battery performance and safety. Apart from active cooling systems, passive cooling systems using PCM matrix are available, particularly for batteries [50–52]. The PCM integrated into the cell and/or battery acts as a heat sink for heat generated and prevents the module temperature from rising sharply. The heat stored can warm the batteries during battery charge or under cold weather conditions. An ideal candidate for PCM cooling should have a melting point between 30 and 60 °C, high latent heat per unit mass and a narrow melting temperature range. Paraffin wax is a good candidate because of its low cost and chemical stability. Other materials used are mixtures of chlorobenzene and bromobenzene [53] and stearic acid [54]. PCMs are also effective in preventing thermal runaway caused by a single cell that has reached a catastrophic failure condition [52].

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