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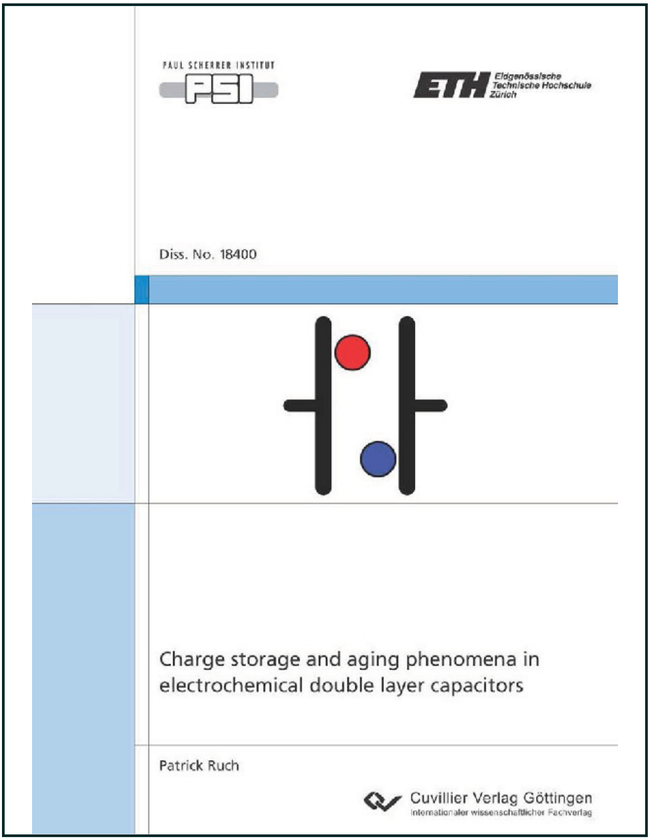
Charge Storage and Aging Phenomena in Electrochemical Double Layer Capacitors



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Chapter 1.

Motivation and scope

1.1. General introduction

There are two prominent challenges facing the global energy economy in the present century. First, the continued depletion of economically viable supplies of fossil fuels is irreconcilable with the significant increase in the world energy consumption [1, 2]. Second, the anthropogenic emissions are, for the first time, of equal magnitude as the natural fluxes and are therefore expected to have a notable impact on the global climate [3]. Thus, it is essential for future energy economies to feature an increased contribution from renewable energy technologies and improved means for efficient energy storage.

As electrical energy storage devices, electrochemical double layer capacitors (EDLCs) can provide valuable contributions to the power quality of grids based on decentralized electricity production as well as to the efficiency of portable and mobile applications which rely on electrical energy. A summary of the properties and application fields of EDLCs is given in Chapter 2. In this context, the limited energy density of EDLCs will be identified as a key weakness of the technology.

By describing the scientific principles underlying the electrochemical energy storage in EDLCs in Chapter 3 and reviewing the properties of the most important electrode material, carbon, in Chapter 4, strategies for increasing the energy density of EDLCs can be outlined. In describing the most promising approaches, the necessity for a more detailed understanding of the charge storage and aging mechanisms of EDLCs at elevated voltages becomes apparent (Chapter 5). An investigation into these mechanisms and their consequences for energy storage in EDLCs is the focus of the present work.

1.2. Scope of this work

An increase in the specific energy of EDLCs is a key research area for the advancement of this electrochemical energy storage technology. A promising approach to achieve this goal is an increase in the device voltage (Chapter 5). However, under these conditions, a significant reduction in the lifetime of EDLCs occurs (Section 5.2.2).

The aim of the present work was to identify the dominant aging mechanisms of EDLCs based on non-aqueous electrolytes in order to describe the processes which lead to performance loss over time at elevated device voltages. Hence, two main experimental strategies were pursued:

1. in situ investigations of potential-dependent structural changes of carbonaceous electrodes, and
2. electrochemical aging of laboratory-scale EDLCs and correlation of the performance loss of single electrodes with the according structural changes.

As reviewed in Section 5.2.2, the majority of irreversible charge loss at elevated voltages does not appear to contribute towards the formation of gaseous reaction products. Hence, no investigations into the gas evolution or pressure build-up in EDLCs were performed in the present work. Also, the influence of temperature on the aging mechanisms of EDLCs was not studied as it does not directly contribute towards an increase in specific energy.

Instead, the experimental efforts focused on less established research areas such as the in situ investigation of the electrochemical charging mechanism in highly porous activated carbon electrodes, dimensional changes of such electrodes as a consequence of electrochemical charging, and the deposition of insoluble electrolyte degradation products on such electrodes. The experimental techniques employed in these studies are described in Part II of this thesis, while the according results are presented in Part III under the following classification:

- characterization of an activated carbon, YP17, in terms of structure, porosity and electrochemical performance in EDLC electrolytes (Chapter 9),

- study of the reversible electrochemical doping mechanism of this carbon and comparison with a model carbonaceous electrode consisting of single-walled carbon nanotubes using in situ Raman spectroscopy and resistance measurements (Chapter 10),
- investigation of the dimensional changes during electrochemical charging of YP17 and single-walled carbon nanotubes via electrochemical dilatometry, as well as of graphite via electrochemical dilatometry and in situ X-ray diffraction (Chapter 11),
- assessment of irreversible changes on the length scale of the microporosity of YP17 using in situ small-angle X-ray scattering (Chapter 12),
- study of solid deposits on a model carbonaceous electrode, highly oriented pyrolytic graphite, after electrolyte degradation at elevated negative and positive potentials, respectively, using atomic force microscopy and X-ray photoelectron spectroscopy (Chapter 13), and
- effects of elevated float voltages on the single electrode capacitance and electrochemical performance of YP17, as well as an ex situ characterization of these electrodes following aging at elevated voltages (Chapter 14).

Each of the chapters listed above contains a concluding section in which the relevant results are briefly summarized. Finally, in Part IV, the insights gained by the various approaches are combined to enable a more complete description of the electrochemical charging and aging of EDLCs based on non-aqueous electrolytes.

Chapter 2.

Practical aspects of energy storage in EDLCs

2.1. Electrical energy storage systems and their applications

The importance of electrical energy has been rising steadily over the past century. While the global consumption of electrical energy was 9.4 % of the world total final energy consumption in 1973, this figure rose to 16.7 % in 2006 [1] and is expected to increase at an even faster rate in future years [4]. This prognosis results from several aspects:

- the rising importance of renewable energy technologies in order to provide a sustainable energy economy which is neutral in anthropogenic emissions,
- the increased use of electrical devices in both industrial and consumer applications, and
- the prospect of zero emissions during local consumption of electrical energy.

Many forms of renewable energy (wind, wave, tidal, solar and run-of-river hydro) result in an electrical energy output which is intermittent or at least variable according to the availability of the resource [5, 6]. Given the importance of a reliable supply of electric power within a stable power network, the need for efficient electrical energy storage techniques is evident.

In Figure 2.1, an overview is given of different electrical energy storage systems currently used in stationary applications for power grids. The wide range of energy content and power output can be explained by the different purposes these systems serve in the context of grid electricity. While pumped hydro, compressed air energy storage (CAES) and flow batteries are best suited for high-energy storage applications (in the order of MWh to GWh), conventional electrochemical batteries and superconducting magnetic energy storage (SMES) are preferred for small and intermediate energy storage systems (few kWh to several hundred kWh).

EDLCs, along with flywheels, fill a particular niche in the context of grid electricity management due to their high efficiencies, high power capabilities and long cycle lives (up to several 10^6 cycles) [4, 8]. Both systems have the disadvantage of energy losses over time with initial rates of ca. 50 % per day for flywheels due to friction and ca. 5 % per day for EDLCs due to electrochemical discharge [4]. Both figures are unsuitable for long-term energy storage. However, EDLCs and flywheels are ideal for power quality management in the form of load leveling during peak power demand, where power in the order of MW needs to be supplied in the time frame of seconds to minutes (Figure 2.2). Regarding applications in which such power capability is the key performance parameter, EDLCs are usually the most cost-effective energy storage (Figure 2.3).

In portable and mobile applications which rely on an integrated or on-board source of electrical energy, it is usually necessary to consider the energy and power content of energy storage devices normalized to their mass or volume in a Ragone plot [9, 10]. In Figure 2.4, the maximum specific power and energy which are obtained with EDLCs at the present state of technology are compared to the corresponding values for other capacitor types and a series of common batteries. For sake of comparison, fuel cells and the internal combustion engine (ICE), which are both energy conversion systems, have also been included in the Ragone plot. In the case of the latter two, the specific properties depend directly on how the fuel is stored prior to conversion within the device itself.

From Figures 2.2 and 2.4, it is clear that EDLCs fill a particular energy storage niche in which power pulses need to be supplied for durations of a few seconds or tens of seconds. Such power demand is required for a range of different systems covering a wide span of total energy content, which has led to the implementation of EDLCs in a number of applications as diverse as memory backup in consumer electronics [11],

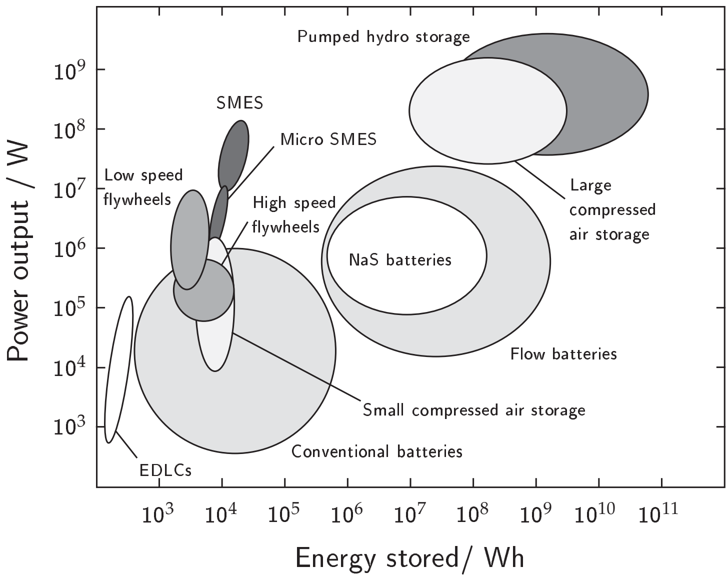

Figure 2.1.: Electrical energy storage systems for grid applications according to their energy content and power output. Adapted from [4].

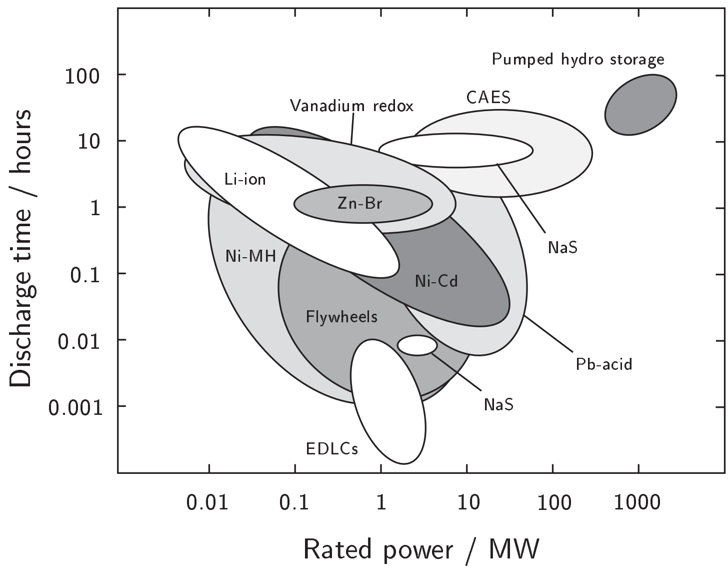

Figure 2.2.: Characteristic discharge time for electrical energy storage installations with varying power ratings as of 2008. Adapted from [7].

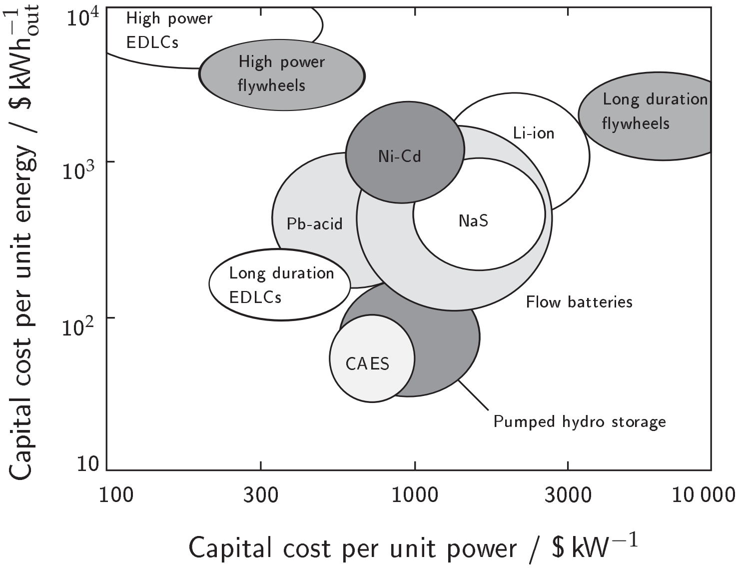

Figure 2.3.: Capital cost per unit energy and power for different electrical energy storage systems. Adapted from [7].

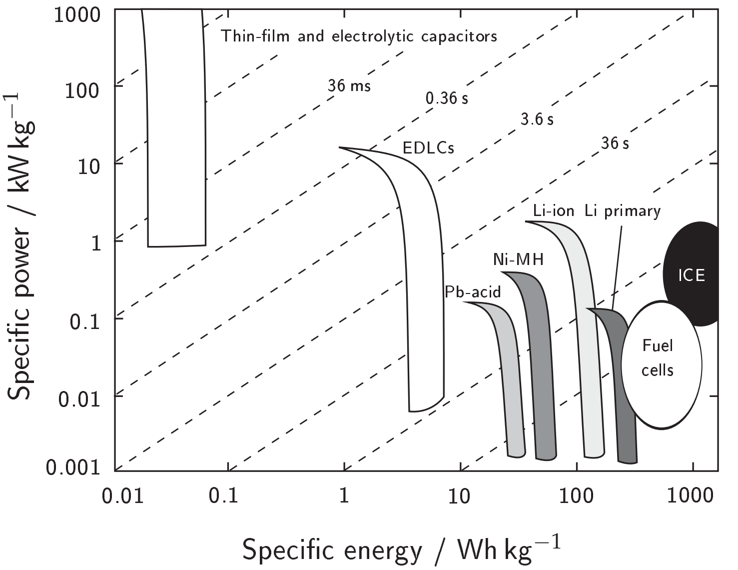

Figure 2.4.: Schematic Ragone plot for EDLCs in relation to other energy storage and conversion devices. The dashed lines indicate time constants for certain combinations of energy and power. Adapted from [4, 11–15].

energy recuperation and boost in electric vehicles [16–20], and load leveling in decentralized power microgrids [21]. A selection of these applications, which vary in maturity from the stage of single prototypes to the extent of mass production, is given in Table 2.1.

In most applications, EDLCs supply the peak loads and act complementary to high-energy storage or conversion devices which supply the bulk of the energy demand. This combination of energy sources which are effective on different timescales permits a downscaling of the primary energy source and thereby improves the overall energy efficiency and cost. Similarly, short interruptions in the main power supply can be compensated through EDLCs which provide the necessary bridge power, thus forming an uninterruptable power supply (UPS). In many cases, peak power loads can be detrimental when applied to a single high-energy device (such as an electrochemical battery), leading to the advantage of a prolonged lifetime of the primary energy source when combined with EDLCs.

In the context of public and individual transport, EDLCs possess a number of advantageous characteristics. They can be both charged and discharged at high rates with high efficiency and cycle life irrespective of their actual state-of-charge, which does not hold for high-power batteries. Thus, they are suitable for repeated recuperation and delivery of

Table 2.1.: Applications of EDLCs listed according to their approximate maximum energy content.

Stored energy	Application	Function	Ref.
< 1 mWh	Consumer electronics	Memory backup	[11]
< 100 mWh	Wireless sensor nodes	Energy harvesting	[22]
0.5–5 Wh	Power tools	Main power source	[23]
	Electric scooters	Peak load supply	[24]
5–20 Wh	Hybrid vehicles	Start-stop	[16]
50–250 Wh	Wind turbines	Blade rotation	[25]
	Hybrid vehicles	Power assist	[16–18, 26]
250–500 Wh	Trolley buses	Recuperation	[27]
	Microgrids	Power quality	[28–30]
> 1 kWh	Light rail vehicles	Recuperation	[31–33]
	Gantry cranes	Recuperation	[23, 34]

energy as is the case for successive deceleration and acceleration cycles in electric vehicles (regenerative braking) [11, 26]. Also, the determination of the state-of-charge of EDLCs is uncomplicated since the voltage of EDLCs increases roughly linearly with increasing state-of-charge (Chapter 3), which facilitates power management significantly. EDLCs using acetonitrile-based electrolytes (Section 3.4) retain their properties down to -40 °C [35], making them ideal for cold starting of engines.

Finally, it must be emphasized that future applications for EDLCs are closely linked to the necessity of electrical energy storage. Given the above prospects in stationary as well as in mobile applications, an increase in the importance of energy storage systems in general and of EDLCs in particular can be expected.

However, despite the various successful applications listed in Table 2.1, the low energy density of EDLCs remains a key limitation which hinders their widespread implementation, as will be briefly highlighted in the next section.