Shift to Post-Li-Ion Capacitors: Electrochemical Behavior of Activated Carbon Electrodes in Li-, Na- and K-Salt Containing Organic Electrolytes

Dominik Stepien,1 Zijian Zhao,1 and Sonia Dsoke 1,2,∗

1Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
2Helmholtz-Institute Ulm for Electrochemical Energy Storage (HIU), D-76021 Karlsruhe, Germany

The interest in exploring intercalation-based energy storage systems, which can be alternatives to the well-established Li+-based systems, is exponentially growing in the scientific community. This shift involves pure battery and hybrid battery-capacitor systems, which contains, at the same time, faradaic-type and double layer-type materials. In order to assess the feasibility of such hybrid system, the single materials have to be firstly analyzed independently. In this work, a commercial activated carbon is taken as an example of double layer-type material and is electrochemically investigated in several organic electrolytes with salts composed of various cations (Li+ , Na+ and K+) and anions (PF6− , TFSI− and FSI−). The adsorption of these cations/anions on the activated carbon and their kinetic properties are studied by means of cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy. Finally, the effect of the different cations on ageing mechanism of symmetric capacitors is studied. The results reveal that the ageing mechanism induced by the Li-salts is different from those achieved with analogue salts containing Na and K cations.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.092181jes]

Manuscript submitted July 17, 2018; revised manuscript received August 14, 2018. Published August 29, 2018.

Experimental

Electrodes preparation.—A commercial activated carbon (Hay-Carb PLC) which was extensively characterized in previous works21,22 was employed as active material for both positive and negative electrodes. This activated carbon has a BET surface area of 1705 m2 g−1 and a meso- and micropore volumes of 0.281 and 0.646 m3 g−1, respectively. The average pore diameter is about 1.2 nm.21 The working electrodes were prepared by mixing activated carbon as active material, SuperP (Imerys) as conductive additive and Na-alginate (Sigma Aldrich) as binder in the mass ratio of 85:5:10. Firstly, the binder solution was prepared by dissolving 2 wt% of Na-alginate in water and further stirred for 3 hours. The final slurry was coated onto an Al foil using doctor blade technique with a wet thickness of 150 μm. The casting layers were slowly dried at room temperature in order to prevent any cracks. Circular electrodes (with 12 mm diameter) were punched out from the layers. The final electrodes have a thickness of 60 ± 5 μm and an active material mass loading of 1.6 ± 0.2 mg.

It is well recognized that electrochemical double layer capaci-
tors (EDLCs) are able to provide exceptionally high power but they suffer of very low energy.1,2 This is the reason that stimulates the research and industry communities to find solutions to enhance the energy density of supercapacitors without sacrificing their excel-
ent power capability and cycling stability. Increasing the cell voltage and enhancing the capacitance of the double layer-type material (generally carbonaceous materials) are some of the strategies adopted so far.2,3 Another approach is to introduce materials which can provide extra energy storage through a fast faradaic process, like the so called “pseudocapacitive” materials.4,5 In this context, the combination of pseudocapacitive-type and double layer-type materials leads to a “hybridization”.6,7 However, the hybridization is not limited to the use of only pseudocapacitive-type materials. A large variety of faradaic compounds which behave more like a battery have also been explored in combination with double layer-type materials.7 Among various possibilities, the most appealing solution is to use materials which can reversibly intercalate and de-intercalate lithium in their structure at various potentials as negative or positive electrode. The combination of the Li-insertion type material and the double layer-type material constitutes the so called Li-ion capacitor (LiC).8,9 LiCs can be considered as a reasonable compromise between two well-known and mature technologies: EDLCs and Li-ion batteries (LiBs). So far, many materials’ combinations have been tested for developing LiCs, resulting in different types of hybridization. The simplest hybridization is the “asymmetric” configuration, where one electrode is a pure Li-insertion type material (e.g. Li4Ti5O12 or Li1.2V2(PO4)3) and the other one a pure double layer-type material (e.g. activated carbon).3,5,6 Another option to design a high performance LiC is to combine two or more different active materials in one electrode, in which different energy storage mechanisms will occur simultaneously, thus developing a “multifunctional” electrode (a bi-material electrode).10,11 In the multifunctional electrode, the double layer-type material (e.g. activated carbon) enables to support high currents and at the same time the Li-insertion type material ensures enough capacity. The proper combination and ratio among the materials are crucial and can drastically affect the electrode performance.11

However, due to the high cost and low abundance of lithium in the earth crust, other alternative chemistries are urgently required. Sodium, the closest element to lithium in the periodic table has been proved as an alternative intercalative ion in battery materials in the past years.12–14 Indeed, due to its abundance and non-toxicity, Na can offer more cost-effective and environmentally friendly energy storage systems. Although it seems that the closest neighbor element is the best choice for lithium replacement because of its similar properties, K is indeed also a competitive option.15–17 A key benefit of potassium batteries is the exceptionally negative potential of the K+/K redox couple which would theoretically enable high energy.15 Another advantage of potassium is its weaker solvation energy with respect to Li and Na, which can result in a higher transport number and therefore an increased power performance.18 Na- and K-ion capacitors are indeed attractive alternatives to LiC.9,19,20 However, in order to design a full hybrid device, it is crucial to investigate the aspects related to each single electrode component in the given electrolyte. If activated carbon will be used in a hypothetical “multifunctional electrode”, its interactions with the given electrolyte have to be studied separately.21

For this purpose, this work focuses on the electrochemical performance of a commercial activated carbon in various electrolytes containing Li-, Na-, and K- salts. This study opens up novel perspectives to a possible development of Na- and K-ion hybrid capacitors containing activated carbon as a part of the electrodes.

* Electrochemical Society Member.

† E-mail: sonia.dsoke@kit.edu
electrodes were finally dried at 120 °C under vacuum for 72 hours in order to remove traces of water.

**Electrolytes.**—Each electrolyte consisted of an alkali salt dissolved in propylene carbonate at the concentration of 0.8 M. Table I gives a list of all electrolytes investigated in this work. In case of TFSI− and FSI−-based electrolytes, 1 wt% of PF6−-based salt was added, in order to avoid the Al-corrosion at anodic potentials.23,24

| Electrolyte         | Abbreviation | Electrolyte Abbreviation |
|---------------------|--------------|--------------------------|
| 0.8 M LiPF6/PC      | LiPF6        | 0.8 M LiTFSI/PC          | LiTFSI      |
| 0.8 M LiTFSI/PC     | LiTFSI       | 0.8 M NaPF6/PC           | NaPF6       |
| 0.8 M NaPF6/PC      | NaPF6        | 0.8 M NaTFSI/PC          | NaTFSI      |
| 0.8 M KPF6/PC       | KPF6         | 0.8 M KTFSI/PC           | KTFSI       |
| 0.8 M KFSI/PC       | KFSI         | 0.8 M LiPF6/PC           | LiPF6       |
|                     |              | 0.8 M KFSI/PC            | KFSI        |

The conductivity of the electrolytes was measured with a Mettler Toledo conductometer at 23 °C.

**Cell assembly.**—Swagelok-type cells with three or two-electrodes configuration have been used for the electrochemical experiments. In the 3-electrode configuration cell, two identical AC electrodes were used as positive and negative electrodes, while metallic lithium, sodium or potassium were used as reference electrode in order to monitor the potentials of positive and negative electrodes during the experiments. The two AC electrodes were separated by two glass microfiber filter separators (Whatman GF/A, Aldrich) and the cell was finally fully-filled with electrolyte. The 2-electrode cells were built with similar configuration with 3-electrode cells, but without the reference electrode.

**Electrochemical characterization.**—It is important to mention that the reference electrodes used here consist of metallic Li, Na and K. As known that Na and K are more reactive than Li, we have monitored the stability of the K electrode (which is the most reactive metal) versus the couple Fc/Fc+ (details can be found in supporting information, S1). For each electrolyte system, a protocol (depicted in Schematic 1) including electrochemical impedance spectroscopy (EIS), cyclic voltammetries (CVs) and galvanostatic cycling with potential limitation (GCPL), was conducted. The cell used for this experimental protocol was a 3-electrode configuration-type.

Floating tests were performed on 2-electrode type cells (without reference electrode) by keeping a constant cell voltage at 2.8 V for 270 hours. Every 10 hours the performance of the AC/AC capacitors were verified by means of 5 galvanostatic cycles conducted at the low current of 0.5 A g−1 and EIS.

EIS measurements were performed by applying a low amplitude alternating voltage of 5 mV at OCV or at 0 V bias cell voltage. The frequency was set in the range of 500 kHz - 10 mHz. The impedance spectra were analyzed and fitted with Relaxi3 software (rdh Instruments). In the protocol represented in Schematic 1 the CVs were carried out with a scan rate of 10 mV sec−1 between 0–2 V. GCPL was carried out at various specific currents ranging from 0.1 to 10 A g−1 (5 cycles for each current) in the same voltage range. The specific current was calculated by considering the active material mass of both electrodes. The capacitance values are referred to the sole active material in one electrode. The test cells were placed in a climate chamber at 25 °C and the electrochemical measurements were performed with a VMP3 multi-channel potentiostat/galvanostat (Bio-logic Science Instruments, France), equipped with an EC-Lab software.

**Results and Discussion**

**Electrochemical characterization of AC/AC capacitors in all electrolyte combinations.**—As depicted in the Schematic 1, the CVs and EIS were recorded on fresh and cycled electrodes. No differences are evident, for this reason only one set of experiments will be shown here.

Fig. 1 shows the cyclic voltammograms of fresh AC//AC capacitors recorded at 10 mV s−1 in all electrolytes under investigation. The maximum cell voltage was set in the safe range of 2 V in order to avoid any possible side reaction due to the nature of the different electrolytes. Thanks to the presence of the reference electrode, it is possible to plot not only the variation of the cell voltage but also the potential of single electrodes versus the specific pseudoreference (M/M2+, where M = Li, Na or K). The voltammogram of the cell (Fig. 1a) does not apparently change by employing different electrolytes. In all cases, the CV response is quasi-rectangular without any faradaic peak, indicating a pure double layer energy storage mechanism. However, depending on the electrolyte used, the profiles of positive and negative electrodes show a certain potential swing asymmetry (Figs. 1b–1h)). The highest asymmetry is displayed in LiPF6-based electrolyte system, while a nearly perfect symmetry is obtained with KTFSI-electrolyte. This asymmetry originates from the difference in capacitance, which depends on the adsorption of the specific cation and anion on the surface of the negative and positive electrode, respectively.

Indeed, the charge accumulated on one electrode is related to the capacitance and the potential through the following equation:

\[ Q = C \Delta V \]  

[1]

For the principle of electro-neutrality, the charge accumulated on the positive and negative electrodes must be equal:

\[ C_+ \Delta V_+ m_+ = C_- \Delta V_- m_- \]  

[2]

where \( C_+, \Delta V_+, \Delta V_-, m_+ \) and \( m_- \) are the capacitances, the potential differences and the active masses of positive (where the anion is adsorbed) and negative (where the cation is adsorbed) electrodes, respectively.

Schematic 1. Experimental protocol used for the electrochemical measurements.
From Eq. 2 it is clear that if the masses of the two electrodes are identical and the capacitances are different, the difference in potentials has to vary in order to maintain the electro-neutrality.

By keeping in mind these considerations, it is possible now to calculate the ratio $C_+/C_-$, whose values are graphically reported in Fig. 2.

If the ratio $C_+/C_-$ is $>1$, the adsorption of the anion on the positive electrode is dominant with respect to the adsorption of the cation on the negative one and vice-versa. From Fig. 2 it is clear that in the cases of electrolytes containing potassium, the asymmetry is less pronounced and the ratios are close to 1. This result suggests that the adsorption on the negative electrode (i.e. the capacitance accumulated at the negative electrode) follows the trend $K^+ > Na^+ > Li^+$. This trend can be correlated to two main factors: (1) the different size of the solvated ions and (2) their different de-solvation energies. Regarding the factor (1), it is well known that the radii of solvated alkali-ions is opposite to the radii of naked ions (see Table II). Considering the factor (2), it is known that larger cations have lower solvation energy respect to smaller cations and it is plausible that they can enter the smaller pores partially de-solvated, thus optimizing the capacitance.

On the other hand, the $C_+/C_-$ values for KPF$_6$, KTFSI and KFSI are similar. No apparent differences can be observed in relation to the different anions.

According to the Schematic 1, the symmetric AC//AC cells were further cycled at different specific currents, from 0.1 to 10 A g$^{-1}$. At low current, all cells deliver the same capacitance of 90 F g$^{-1}$. On the other side, relevant differences can be observed at high specific currents.
Figure 3. (a-c) Rate capabilities of symmetric AC//AC capacitor cells in all electrolytes and (d) the related galvanostatic profiles at 10 A g\(^{-1}\).

The differences in rate capabilities are related to the differences in resistances of the various AC//AC systems. The iR-drop, which can be visualized as the potential difference obtained when the sign of the current changes (Fig. 3d), represents the total resistance of the cell, which is the sum of many contributions, like the contact resistance, the resistance of the electrolyte in the cell bulk and inside the pores of the activated carbon. A very powerful tool to analyze and separate the various resistance contributions is the EIS technique. As depicted in the Schematic 1, EIS were recorded on fresh and cycled cells. Since no apparent differences were noticed between these two experiments, only one set of EIS data was analyzed.

All spectra shown in Fig. 4 display similar main features. The intercept at high frequencies represents the resistance of the electrolyte in the cell bulk. At the high to medium frequencies (from 500 kHz to 200 Hz) it is possible to detect different resistance sources: the contact resistance (electrode-current collector and particle-particle contact) and the resistance due to the presence of a solid permeable interface (SPI). This interface is often called solid electrolyte interface (SEI). However, SEI is normally formed on negative electrodes at potentials lower than 1 V vs. Li/Li\(^+\)) and it is due to the electrochemical reduction of the electrolyte on the electrode surface. On the contrary, the SPI is much thinner passivation layer, formed at positive electrodes in Li-ion batteries and on high surface capacitor-type materials.\(^{25-29}\) These two phenomena occur in very close frequency regions and, for this reason, they often result in two overlapped semicircles. At lower frequencies, a diffusion-like behavior can be recognized as a 45° sloped line. The physical meaning of this 45° branch (generally associated to the so called Warburg element) for supercapacitors can be explained as the pore diffusion.\(^{30}\) On the other side, for intercalation type materials the same feature represents a solid diffusion in the particle bulk.\(^{31}\) After crossing a characteristic frequency (the so called “knee-point”, indicated in Fig. 4d) all spectra show a capacitive-like branch, viewed as a quasi-vertical line, which is nearly parallel to the imaginary axis. The frequency at the “knee-point” is an indicator of how fast the capacitor can be charged and discharged and its corresponding time is also indicated as \(\tau\) (“relaxation time”, also called “time constant”). The spectra were fitted by using the equivalent circuit shown in Fig. 4d. We used the finite Warburg-Impedance element (Warburg Open, indicated as Wo) to fit the diffusion and capacitive parts.

In this context, the goal is to understand the transport of electrolytes, based on the combination of different cations and anions, in the micropores of the activated carbon. This effect can be highlighted by the “pore resistance” parameter (R\(_{pore}\) calculated from the Wo, details in supporting information). In Fig. 5 it is possible to observe that the pore resistance follows the same trend as the resistance of the “free” electrolyte in the cell bulk (R\(_{el}\), resistance of the electrolyte). Both these two parameters decrease in the order Li > Na > K. Here, the key-factor is not only the nature of the cation, also the anion used plays an important role. Indeed, in the case of potassium, the presence of FSI\(^-\) has a great contribution on minimizing the resistances. These trends perfectly reflect the respective electrolyte conductivities...
Figure 4. (a, b and c) Nyquist plots of symmetric AC//AC capacitor cells in the various electrolytes and (d) magnification at high frequencies of one exemplary spectra and equivalent circuit used to fit the Nyquist plots.

Figure 5. Relevant parameters calculated by fitting the spectra of Fig. 4: (a) Pore resistance, (b) resistance of the electrolyte.

(Fig. S2). Higher mobility of the ions in the electrolyte bulk reflects higher mobility inside the activated carbon pores as well.

Open circuit potential evolution during the experimental time.— An important issue that was very recently discussed in literature is the questionable stability of the potential of the activated carbon in Li-salt containing electrolytes. Indeed, Widmaier et al. argued that small cations like H⁺ or Li⁺ can interact with the reactive sites (edge basal plane of graphene layers) and with the functional groups which are present on the surface of activated carbon. The authors explained that the physisorbed cations can act as electron-withdrawing entities, resulting in an increased electrode potential. Among the three cations here studied, Li⁺ is the hardest acid and can interact stronger with the reactive sites and functional groups of AC. Fig. 6 shows the open
circuit potentials (OCV) measured versus the reference electrode (Li, Na or K) of the negative activated carbon electrode in the various electrolytes after each electrochemical experiment conducted in the protocol of Schematic 1. The initial OCV of the AC increases in the order Na < K < Li and perfectly reflects the trend of the potential of the relative redox couples (Na+/Na > K+/K > Li+/Li), indicating that the initial potential of AC is not affected by the cation used.

The observed trend of the drift during the electrochemical protocol follows the order Li > Na > K. This confirms the involvement of the cation on the potential drift, which is mitigated by the presence of bigger cations (i.e. softer acids). Widmaier et al.33 argued that the cation on the potential drift, which is mitigated by the presence of the carbon. The solvation energy of K+ is weaker than that of Li+ and it is more probable that K+ enters the pores without (or at least with a smaller amount of) solvent molecules. For this reason, the probability of reactions in the inner surface is lower with K- respect to Li-.3234 For ideal systems, the slope should be equal to (0.01–0.1 Hz) indicates how much the system deviates from the ideality,3234 For ideal systems, the slope should be equal to 1. Higher values indicate that the pores cannot be completely saturated by the solvent molecules.

As previously reported,35 the analysis of $C''$ vs. log($f$) gives information about the relaxation time ($\tau$). Here $C''$ is the imaginary part of the capacitance and calculated as following:

$$C''(\omega) = \frac{Z''(\omega)}{\omega |Z(\omega)|^2}$$

The graph of $C''$ vs. log($f$) displays a peak at the frequency where the system turns from resistive to capacitive behavior (inset in Fig. 8b). The invers of this characteristic frequency corresponds to $\tau$. In summary, $\tau$ can establish how fast the capacitor can be completely discharged.

Ageing of AC//AC cells under floating conditions at 2.8 V.—To study the behavior under ageing conditions, Li, Na and K electrolytes based on PF6− salts were chosen. TFSI− and FSI− anions were not used in this experiment in order to avoid any possible interference to the ageing due to the Al-corrosion, which can occur in presence of these anions at potentials higher than 4 V vs. Li/Li+. Symmetric AC//AC cells were assembled without reference electrode in order to exclude any degradation process due to the alkali metal decomposition in the long experimental time-scale. In order to accelerate the ageing, the cells were subjected to floating periods by keeping the voltage of the cells at 2.8 V. The performances were evaluated every 10 hours of floating-time by means of galvanostatic cycling, performed at the low current of 0.5 A g−1, and EIS.

No obvious and dramatic loss of capacitance can be observed during 270 h of floating time (Fig. 7a). However, some changes in the galvanostatic profile can be observed in all the three cases (inset of Fig. 7a). The profiles become less symmetric and slightly get deformed respect to the initial ones, indicating some loss in energy efficiency. In fact, as viewed in Fig. 7b, the coulombic efficiency remains near 100%, while the energy efficiency decreases with the ageing time.

EIS gives in-depth information about the phenomena which occurs at the different time domains. From the low frequency part, it is possible to understand if the micro-pores (mainly responsible for the capacitance) are still available for fully storing the electrical charge. The slope of log($-Z''$) vs. log($f$) in the low frequency region (0.01–0.1 Hz) indicates how much the system deviates from the ideality. For ideal systems, the slope should be equal to 1. Higher values indicate that the pores cannot be completely saturated by the ions. These values remain in the range ~0.95—0.96 for all electrolytes at every ageing state, confirming that, at low currents, the whole capacitance can still be reached (Fig. 8a). Only a very slight increase of the slope value can be observed for LiPF6.

As previously reported,36 the analysis of $C''$ vs. log($f$) gives information about the relaxation time ($\tau$). Here $C''$ is the imaginary part of the capacitance and calculated as following:

$$C''(\omega) = \frac{Z''(\omega)}{\omega |Z(\omega)|^2}$$

The graph of $C''$ vs. log($f$) displays a peak at the frequency where the system turns from resistive to capacitive behavior (inset in Fig. 8b). The invers of this characteristic frequency corresponds to $\tau$. In summary, $\tau$ can establish how fast the capacitor can be completely discharged.
charged and discharged. Fig. 8b reports the values of $\tau$ as function of the floating time. A gradual increase with the time can be observed for all capacitors.

This behavior is the obvious consequence of an increase in resistance. The nature of the resistive components, which play a role on slowing down the capacitor, can be understood by fitting the impedance and extracting the key-parameters, which are behind the related physical phenomena.

In agreement with the increase of the time constant, the total resistance (Fig. 9a) also increases with time for all the three AC//AC capacitors and, among the three electrolytes, the same trend as observed on fresh electrodes is still maintained: the electrolyte containing K-salt confers the lowest resistance to the cell at every ageing time. As previously discussed, the total resistance can be divided in three main contributions: the electrolyte resistance, the SPI/contact resistances and the pores resistance (Fig. 9). The resistance of the electrolyte
increases only slightly over time and it is more pronounced for LiPF₆ (Fig. 9b). On the other side, the semicircle at high frequencies sensibly grows, especially for the capacitor aged in NaPF₆. This indicates that some product coming from the electrolyte decomposition contributes to progressively grow the SPI, thus hindering the electrical contacts. The growing trend of the SPI/contact resistance is completely different from what observed for other parameters: the cell containing LiPF₆ shows, in this case, the lowest increase, followed by the one containing KPF₆. The cell aged with NaPF₆ shows the highest SPI/contact resistance overall (Fig. 9c).

The pores resistance (Fig. 9d) is similar in all cases until 80–90 h of ageing. After this time, the Rs related to the cell aged with LiPF₆ increases very fast, while for the other two cells this degradation is smoother. After 270 h of ageing, the Rs related to LiPF₆ is two times higher than the one related to KPF₆ and NaPF₆.

By summing up these results one can conclude that when using LiPF₆ the resistance mainly increases inside the pores, while with NaPF₆ and KPF₆ (especially for NaPF₆) the growth of the high frequency semicircle is predominant. Based on these observations, it is possible to suggest two different mechanisms.

Li⁺, the smallest ion and the hardest acid, enters the pores mostly with its solvation shell. At high cell voltage the electrolyte decomposes. With LiPF₆, the decomposition occurs partially inside the pores of the activated carbon. By keeping in mind that the capacitance at the low frequencies (and at low current in a galvanostatic experiment) is still recoverable, the decomposition does not affect the micropores (which are responsible for the capacitance) but rather the meso-macro pores (which are limiting, instead, the kinetic). In the other two cases (with NaPF₆ and KPF₆) larger and softer-acid cations are involved, which do not transport as much molecules of solvent inside the pores as in the case of lithium. In these cases, the degradation mostly occurs on the external surface by the SPI growing and thus contributing to the decrease of the electrical contact.

Conclusions

With this study, the electrochemical behavior of electrodes prepared with a commercial activated carbon in non-conventional electrolytes based on Li-, Na- and K-salts was systematically analyzed. Electrolytes based on K-salts show clear advantages respect to the others electrolytes in terms of higher ionic conductivity and faster diffusion inside the micropores of the activated carbon. The “softer” character of the large K⁺ with respect to Li⁺ confers several advantages to the system: i) a lower interaction with the active sites of AC, which results in a mitigated potential drift; ii) lower desolvation energy, which results in a higher conductivity. Moreover, it is important to highlight that these properties are not only important for the kinetics, but also for the stability of the cells. Indeed, by a close look to the ageing behavior of AC/AC devices in the electrolytes containing the three cations, it is clear that the ageing mechanism depends on the nature of the alkali cation. Lithium induces a different ageing mechanism than the larger sodium and potassium. With its harder acid character, Li⁺ transports the solvent molecules preferentially inside the pores of the AC, where the decomposition predominantly occurs. On the other side, it is presumable that Na⁺ and K⁺ do not transport a large amount of solvent inside the pores and the decomposition mainly occurs on the external surface of the AC. This finding was demonstrated by analyzing the EIS spectra during ageing. With LiPF₆, the predominant resistance growth is inside the pores (i.e. pore resistance), while with NaPF₆ and KPF₆ the predominant growth occurs outside the pores (i.e. contact resistance and SPI resistance).

Acknowledgments

S.D. gratefully acknowledge the financial support of the Ministry of Science and Art Baden Württemberg (MWK) through the “Brigitte-Schlieben-Lange Programm”.

ORCID

Sonia Dsoke https://orcid.org/0000-0001-9295-2110

References

1. P. Simon and Y. Gogotsi, Nature Materials, 7, 845 (2008).
2. Y. Wang, Y. Song, and Y. Xia, Chem. Soc. Rev., 45, 5925 (2016).
3. J. Glanfield, R. Bouchal, E. Mourad, M. Olarte, S. le Vot, F. Favier, and O. Fontaine, Journal of The Electrochemical Society, 165 (3), A657 (2018).
4. V. Augustyn, P. Simon, and B. Dumm, Energy Environ. Sci., 7, 1597 (2014).
5. B. E. Conway, V. Birrs, and J. Wojtowicz, Journal of Power Sources, 66, 1 (1997).
6. Jinfeng Sun, Chen Wu, Xiaofei Sun, Hong Hu, Chunjy Zhi, Limrui Hou, and Changzhou Yuan, J. Mater. Chem. A, 5, 9443 (2017).
7. Z. Zhao, R. Li, C. Zhou, Y. Li, J. Xia, and J. Liu, Adv. Sci., 4, 1600539 (2017).
8. K. Naoi, S. Ishimoto, J.-i Miyamoto, and W. Naoi, Energy Environ. Sci., 5, 9363 (2012).
9. S. Dsoke, B. Fuchs, E. Gucchiardi, and M. Wohlfahrt-Mehrens, Journal of Power Sources, 282, 385 (2015).
10. D. Cerioli, P. Novák, A. Wokan, and R. Kötz, J. Power Sources, 196, 10305 (2011).
11. M. Scичiarioli, R. Marassi, M. Wohlfahrt-Mehrens, and S. Dsoke, Electrochimica Acta, 210, 425 (2016).
12. J.-Y. Hwang, S.-T. Myung, and Y.-K. Sun, Chem. Soc. Rev., 46, 3529 (2017).
13. Z. Dai, U. Mani, H. T. Tan, and Q. Yan, Small Methods, 1, 1700098 (2017).
14. Y. Luo, Y. Tang, S. Zheng, Y. Han, X. Xue, and H. Pang, J. Mater. Chem. A, 6, 4236 (2018).
15. A. Elchehri, Z. Jian, and X. Ji, ACS Appl. Mater. Interfaces, 9, 4407 (2017).
16. J. C. Pramudita, D. Sehrawat, D. Gooenettleke, and N. Sharma, Adv. Energy Mater., 7, 1602911 (2017).
17. X. Wu, D. P. Leonard, and X. Ji, Chem. Mater., 29, 5031 (2017).
18. S. Komaba, T. Hasegawa, M. Dabhi, and K. Kubota, Electrochemistry Communications, 60, 172 (2015).
19. H. Wang, C. Zhu, D. Chao, Q. Yan, and H. J. Fan, Adv. Mater., 29, 1702093 (2017).
20. A. Le Comte, Y. Reymer, C. Vincens, C. Ley, and P. Azais, Journal of Power Sources, 313, 282 (2016).
21. T. Zhang, B. Fuchs, M. Scичiarioli, M. Wohlfahrt-Mehrens, and S. Dsoke, Electrochimica Acta, 218, 163 (2016).
22. H. Y. Tran, M. Wohlfahrt-Mehrens, and S. Dsoke, Journal of Power Sources, 342, 301 (2017).
23. K. Furukawa, N. Yoshimoto, M. Egashira, and M. Morita, Electrochimica Acta, 140, 125 (2014).
24. M. Dabbi, F. Ghamouss, P. Tran-Van, D. Lemordant, and M. Anouti, Journal of Power Sources, 196, 9743 (2011).
25. Y. Matsuda, H. Nakashima, M. Morita, and Y. Takasu, J. Electrochem. Soc., 128, 2552 (1981).
26. Tuan Anh Pham, Kyoung E. Kweon, Amit Samanta, Vincenzo Lordi, and John E. Pask, J. Phys. Chem. C, 121, 21913 (2017).
27. K. Edström, T. Gustafsson, and J. O. Thomas, Electrochimica Acta, 50, 397 (2004).
28. Nellymari Membreneo, Kyusung Park, John B. Goodenough, and Keith J. Stevenson, Chem. Mater., 27, 3332 (2015).
29. Weiwei Qu, Enkhbatul Enkhjav, Rajafekhan Rajagopalan, and Clive A. Randall, Chem. SciChinA, 11, 1162 (2014).
30. S. Dsoke, X. Tian, C. Taibert, S. Schlüter, and M. Wohlfahrt-Mehrens, Journal of Power Sources, 238, 422 (2013).
31. M. D. Levi and D. Aurbach, J. Phys. Chem. B, 101, 4630 (1997).
32. T. Zhang, B. Fuchs, M. Scичiarioli, M. Wohlfahrt-Mehrens, and S. Dsoke, Electrochimica Acta, 218, 163 (2016).
33. M. Widmaier, B. Krüner, N. Jackel, M. Aslan, S. Fleischmann, C. Engel, and V. Presser, Journal of The Electrochemical Society, 163 (14), A2596 (2016).
34. Ann Laheär, Aalari Jännes, and Enn Lust, Electrochimica Acta, 56, 9048 (2011).
35. P. L. Taberna, P. Simon, and J. F. Favier, Journal of The Electrochemical Society, 150 (3), A292 (2003).