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Redox activity of pseudohalides in electrochemical capacitor application

Aktywność redoks pseudohalogenków w kondensatorach elektrochemicznych

DOCTORAL DISSERTATION

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> *"If you want to build a ship, don't drum up people to collect wood and don't assign them tasks and work, but rather teach them to long for the endless immensity of the sea."*
> Antoine de Saint-Exupery

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> *"It always seems impossible until it's done."*
> Nelson Mandela

ABSTRACT

Growing demand for energy and society's expectations regarding portable devices and electric/hybrid vehicles imposes the development of the energy storage/conversion devices market. Therefore, it is necessary to look for better, longer-lasting, and reliable solutions. There is a great diversity in energy storage/conversion devices and depending on the user needs, one can choose over batteries (primary and secondary ones), solar cells, fuel cells, capacitors and electrochemical capacitors. Despite the broad spectrum of devices available, still a huge potential for electrochemical capacitors improvement is seen. These devices are characterized by tremendous power but moderate energy is their limiting factor. This work tries to address these challenges and is thus focused on the development of electrochemical capacitors.

The dissertation is divided into three main parts. The first part – **Chapter I**, includes the literature review concerning the basics of electrochemical capacitors – their construction, commonly used materials and mechanism of charge storage. Special attention is paid to electrolytes for electrochemical capacitors due to many different types of electrolytes that can be distinguished, strongly influencing the performance of these devices. Moreover, there are promising perspectives of using new electrolytic solutions in order to improve the operating parameters of the electrochemical capacitors.

The second part – **Chapter II**, presents the summary of the papers (**P1-P4**) concerning **the redox-active solutions applied as electrolytes in electrochemical capacitors.** Systems operating with aqueous solutions, as well as the ionic liquid, containing pseudohalide anions (thiocyanate and selenocyanate) are investigated. In the case of the aqueous medium, salts of various alkali metals are tested. Moreover, the impact of solution concentration on their physical and electrochemical properties is also defined. The electrochemical behavior of the cells is investigated for two types of electrode materials (entirely microporous and micro/mesoporous) and current collectors (stainless steel *vs.* gold for aqueous solutions and stainless steel *vs.* aluminum for the ionic liquid). Potassium thiocyanate-based aqueous electrolytes were further modified with gold nanoparticles to improve the electrochemical capacitor performance.

It is presented that all proposed electrolytes can be successfully used in electrochemical capacitors and significant improvement of their operating parameters is seen. In comparison to one of the most popular aqueous electrolyte for electrochemical capacitors – lithium sulfate solution, the specific energy increased from 8 $\text{Wh}\cdot\text{kg}^{-1}$ to 12 $\text{Wh}\cdot\text{kg}^{-1}$ (for KSeCN solution) and 16 $\text{Wh}\cdot\text{kg}^{-1}$ (for KSCN-based electrolytes). Moreover, due to the presence of gold nanoparticles in the electrolytic solution, power retention is noticed while maintaining high energy values.

In **Chapter III,** the fundamental studies of electrochemical capacitors' charge storage mechanism in the ionic liquid – 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**P5**) and aqueous electrolyte - lithium sulfate solution (**unpublished data**) are described. The experiments were performed with **the electrochemical dilatometer** (coupled with the step potential electrochemical spectroscopy).

In paper denoted as **P5,** two carbon materials of different physical characterization were considered in order to determine the impact of material porosity on the electrical double-layer formation. It was found out that the mechanism of charge accumulation depends on the electrode polarization (whether negatively or positively), noticed as non-symmetric electrode height changes (despite similar anions and cations size of the ionic liquid chosen).

The experiments performed in an aqueous medium were **to evaluate how the pH of the electrolyte impacts the charge accumulation in porous carbon electrodes**. The electrodes were polarized positively and negatively (with different electrochemical techniques) in various electrolytes – 1 $mol \cdot L^{-1}$ Li_2SO_4 solutions of pH 6, 9 and 12. It was concluded that the higher pH of the electrolyte, the bigger the contribution of hydroxide anions in the electric double-layer formation at the electrode polarized positively. Moreover, the electrode height changes recorded in Li_2SO_4 solution of pH 12 are more comparable to the changes obtained in LiOH solution rather than for sulfate-based solutions of lower pH.

STRESZCZENIE

W związku z rosnącym zapotrzebowaniem na energię oraz wymaganiami współczesnego społeczeństwa dotyczącymi urządzeń mobilnych oraz pojazdów elektrycznych /hybrydowych, rynek urządzeń do magazynowania i konwersji energii dynamicznie się rozwija. Konieczne jest zatem poszukiwanie lepszych, trwałych i niezawodnych rozwiązań. Można wyróżnić kilka rodzajów urządzeń do magazynowania/konwersji energii – np. ogniwa (pierwotne i wtórne), ogniwa słoneczne, ogniwa paliwowe, kondensatory czy kondensatory elektrochemiczne, i wybrać odpowiednie, w zależności od potrzeb użytkownika. Kondensatory elektrochemiczne jako urządzenia o ogromnej mocy, ale stosunkowo niskiej energii wymagają poprawy tego ograniczającego je parametru w celu poszerzenia ich możliwości aplikacyjnych. W związku z powyższym, niniejsza praca dotyczy poprawy parametrów pracy kondensatorów elektrochemicznych.

Prezentowana rozprawa doktorska podzielona jest na trzy główne części. Część pierwsza – **Rozdział I**, obejmuje przegląd literaturowy, dotyczący podstawowych zagadnień związanych z kondensatorami elektrochemicznymi – ich budową, powszechnie stosowanymi materiałami oraz mechanizmami magazynowania ładunku. Szczególną uwagę poświecono elektrolitom stosowanym w kondensatorach elektrochemicznych, ponieważ wyróżnić można wiele typów elektrolitów, które w znaczący sposób wpływają na wydajność tych urządzeń. Co więcej, zastosowanie nowych roztworów stanowi obiecujący sposób poprawy parametrów pracy kondensatorów elektrochemicznych.

Część druga – **Rozdział II**, stanowi streszczenie publikacji (**P1-P4**), które dotyczą roztworów wykazujących aktywność redoks zastosowanych jako elektrolity w kondensatorach elektrochemicznych. Zbadane zostały zarówno roztwory wodne jak i ciecze jonowe, zawierające aniony pseudohalogenkowe (tiocyjanioanowe i selenocyjanianowe). W przypadku roztworów wodnych, sole metali alkalicznych zostały wzięte pod uwagę. Dodatkowo, zbadano wpływ stężenia roztworów na ich właściwości fizyczne i elektrochemiczne. Zachowanie elektrochemiczne układów badawczych zostało zbadane przy zastosowaniu dwóch różnych materiałów elektrodowych (mikroporowatego oraz mikro/mezoporowatego) oraz różnych kolektorów prądowych (stali nierdzewnej i złota, w przypadku roztworów wodnych, oraz stali nierdzewnej i glinu dla cieczy jonowej). Elektrolity wodne na bazie tiocyjanianu potasu zostały zmodyfikowane nanocząstkami złota w celu dalszej poprawy parametrów pracy kondensatora elektrochemicznego.

Na podstawie przeprowadzonych badań i uzyskanych wyników wykazano, że zaproponowane elektrolity mogą być z powodzeniem stosowane w kondensatorach elektrochemicznych. Wykazano również znaczną poprawę parametrów pracy tych urządzeń. Porównując wartości energii uzyskiwane w urządzeniach pracujących w jednym z najpopularniejszych wodnych elektrolitów (w roztworze siarczanu(VI) litu) zaobserwowano wzrost tego parametru z 8 $Wh \cdot kg^{-1}$ do 12 $Wh \cdot kg^{-1}$ (dla roztworu KSeCN) i 16 $Wh \cdot kg^{-1}$ (dla elektrolitów na bazie KSCN). Co więcej, dzięki obecności nanocząstek złota w roztworze elektrolitu, obserwuje się utrzymanie wysokich wartości mocy właściwej, przy zachowaniu wysokich wartości energii.

W **Rozdziale III** opisane zostały badania podstawowe, wyjaśniające mechanizmy magazynowania ładunku w kondensatorach elektrochemicznych operujących w cieczy jonowej – bis(trifluorometylosulfonylo)imidku 1-etylo-3-metyloimidazoliowym (**P5**), oraz w elektrolicie wodnym – roztworze siarczanu(VI) litu (**nieopublikowane dane**). Badania zostały wykonane przy użyciu dylatometru elektrochemicznego oraz spektroskopia elektrochemiczna z krokowo zmieniającym się potencjałem. W publikacji **P5** dwa materiały węglowe o różnej charakterystyce zostały wzięte pod uwagę w celu określenia wpływu porowatości materiału na proces tworzenia się podwójnej warstwy elektrycznej. Na podstawie niesymetrycznych zmian wysokości elektrody podczas polaryzacji w stronę potencjałów ujemnych oraz dodatnich, wykazano, że mechanizm magazynowania ładunku zależy od kierunku polaryzacji elektrody (pomimo podobnych rozmiarów anionów oraz kationów wybranej cieczy jonowej).

Badania przeprowadzone w środowisku wodnym miały na celu **ocenę wpływu pH roztworu elektrolitu na magazynowanie ładunku w porowatych elektrodach węglowych**. Elektrody były polaryzowane w stronę potencjałów dodatnich oraz ujemnych (przy zastosowaniu różnych technik elektrochemicznych) w 1 $mol \cdot L^{-1}$ roztworach Li_2SO_4 o różnym pH – 6, 9 i 12. Wywnioskowano, że im wyższe pH elektrolitu, tym bardziej zauważalny jest udział anionów wodorotlenkowych w tworzeniu się podwójnej warstwy elektrycznej przy elektrodzie polaryzowanej dodatnio. Co więcej, zmiany wysokości elektrody zarejestrowane w roztworze Li_2SO_4 o pH 12 są raczej porównywalne do zmian zmierzonych w roztworze LiOH jako elektrolicie, niż do zmian obserwowanych w siarczanowych elektrolitach o niższym pH.

TABLE OF CONTENT

GENERAL INTRODUCTION

Electricity is ubiquitous. Nowadays, most of us are not able to imagine our lives without electricity. Lighting, washing machines, vacuum cleaners, dishwashers, personal computers and laptops, TV sets and mobile phones are used every day to help us with our domestic duties but also to entertain.

It is quite interesting that the principle of static electricity was discovered around 585 BC by Thales of Miletus. Unfortunately, because of the lack of necessary tools, the development in this field began much later, i.e., in the 17th century. At that time, William Gilbert found out that it was possible to charge other objects (not only the amber, as it was discovered by Thales). He used the word *electricity*, meaning "like amber in its attractive properties". Later on, Stephen Gray, who is said to be the father of electricity, discovered that electricity could be transferred from one object to another by using metals or wet fibers. In consequence, he divided materials into electrical conductors and insulators. In the late 18th century, Alessandro Volta invented the voltaic pile which is known as the first electrical battery that provides direct current (DC). Few years after this invention, the very first electrostatic law was formulated by Charles Coulomb. He discovered that the force between two electrical charges is proportional to the product of the charges and inversely proportional to the square of the distance between them. In 1827, Georg Ohm described the relationship between the voltage applied and the electric current. Three years later, Michael Faraday discovered that the current flow is induced by magnet movement close to the spiral-shaped conductor which was described as Faraday's law. Another significant discovery was made by Heinrich Rudolf Hertz who proved the existence of electromagnetic waves and their resemblance to light (the same velocity of these two types of waves). His discovery was crucial and contributed to the development of radiocommunication [1-4].

Although inventions and discoveries related to electricity have occurred throughout many years, taking into account their practical significance, the activities of Thomas Edison and Nikola Tesla seem to be the most impactful.

Thomas Edison invented the incandescent light bulb which was one of the first applications of electricity to modern life (patented in 1880), powered with direct current. Edison believed that DC is safe and he was focused on its development. However, a major issue with DC was the difficulty in converting it into different voltages. It caused, among others, many fires at houses. Additionally, it required a sub-station every 3 km. Nikola Tesla, as a young researcher, was working with Thomas Edison. He invented alternating current (AC) that was believed to solve the problems of DC (voltage could be changed and the electricity could be transported for long-distance without significant voltage loss). This discovery started the conflict between these two great scientists. In the end, nonetheless, it can be said that Nikola Tesla won this conflict and thanks to his invention we can spread energy all over the world and use electricity in our everyday life. But does it mean that direct current is useless nowadays? Of course not. Popular batteries, primary as well as secondary ones, solar power systems, fuel cells and electrochemical capacitors deliver direct current that can be used to power various types of equipment, starting from small electronics, i.e., smartwatches, smartphones, to hybrid electric vehicles, seaport crane or diesel railroad locomotives.

CHAPTER I

Literature review

1. Introduction

The world has been changing rapidly after the invention of electricity. Initially, electricity was used exclusively to power. However, science development shows that electrons and, in consequence, current can transport information. When voltage changes in a conductor, a message can be sent. Based on this knowledge, an electrical telegraph was constructed giving the beginnings for a telephone and a radio. In 1973 a prototype of a mobile telephone was presented [5]. This invention is thought to be a milestone in portable electronics development. These days, it is expected that portable devices will work longer without the necessity to charge them very often. Moreover, when they need to be charged it should not take a very long time. To realize how important this topic is, three great scientists should just be mentioned: John B. Goodenough, M. Stanley Whittingham and Akira Yoshino who have been awarded the 2019 Nobel Prize in Chemistry for the development of lithium-ion batteries that "enabled the mobile world" – as Olof Ramström said. However, lithium-ion batteries are not the only power systems that are used by modern society. Furthermore, they are not the safest possible solution (due to hazardous and flammable solvents) [6, 7].

The energy can be obtained from various sources. In the European Union five major energy sources can be distinguished (presented in Fig. 1).

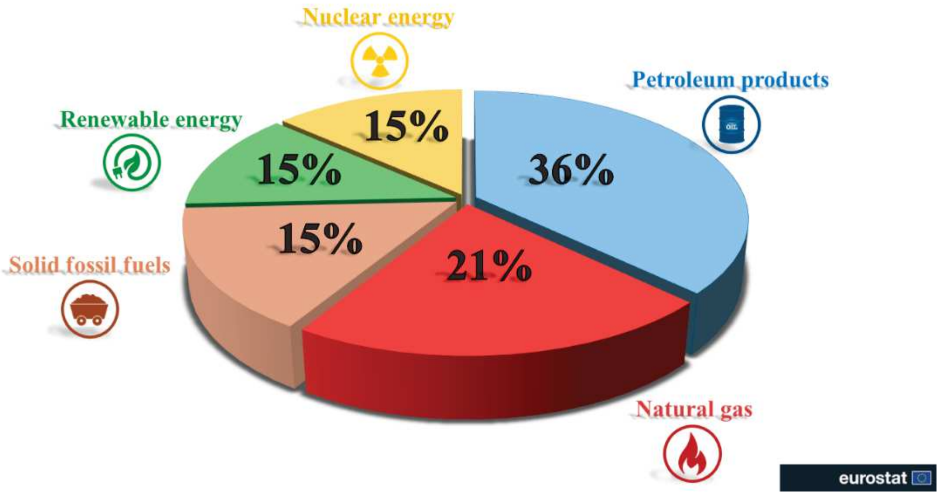


Fig. 1. The energy sources in the European Union (including energy produced and imported) based on Eurostat database

The data presented include the energy produced in the EU and the energy imported. It is clearly seen that the main sources are petroleum products (including crude oil), natural gas and fossil fuels. Unfortunately, these sources are non-renewable and they have been depleting within years. It is thus reasonable that energy will be produced from renewable sources like wind, sun, or water. These sources are not available all the time – there are cloudy or windless days. And even if there is a possibility of, for example, sun energy production during the day, people may want to use it later – in the evening, to lighten their houses. Hence, the energy has to be stored. Electrochemical capacitors (ECs) might come in useful in this case. These devices, commonly available and employed nowadays, still need to be improved, because of their limited performance parameters, especially moderate energy.

2. Electrochemical capacitors

2.1. Capacitors and fundamentals of the energy storage mechanisms

When thinking about electrochemical capacitors, their construction and the principle of operation, one should first get acquainted with conventional capacitors. A capacitor is a device that stores the charge. It consists of two conducting plates with an insulating material (a dielectric) between them. These plates are called electrodes. They have a defined surface area (A) and they are separated in a distance (d). When the external power supply is connected to the capacitor, it forces negative charges (electrons) to move from one plate to the other. Hence, one electrode is negatively charged and the second one is positively charged. Because of a dielectric between them, the negative charges are not able to move back through the capacitor. As a consequence, both plates keep the equal charge of opposite sign creating an electric field between them. Due to the development of the electric field between the electrodes, the electric energy is stored in this field. That is why capacitors are called the energy storage devices [8-10].

Additionally, each plate, having its own charge, affects polar molecules present in the dielectric – they change their orientation according to the electric field, thereby increasing capacitance of the capacitor: the positively charged electrode attracts even more negative charges from the second electrode and pushes away positive charges from its own surface. It means that an appropriately selected dielectric can increase capacitance of the capacitor [10, 11].

When the external power supply is disconnected from the circuit, the fully charged capacitor is able to store this charge for some time. Based on defined values, A (m^2) and d (m), capacitance of the capacitor (C) can be described as follows:

$$C = \frac{\varepsilon_r \cdot \varepsilon_0 \cdot A}{d} \qquad \textbf{eq. 1}$$

showing that the larger the electrode area, the higher capacitance can be reached [12, 13]; as capacitance is inversely proportional to the distance *d* between the plates, with decreasing this distance capacitance increases. The unit of *C* is Farad, F. One should remember, that 1 F, as the SI Unit, is 1 $C \cdot V^{-1}$, which means the number of coulombs stored (total charge, *Q*, C) per 1 V. Based on this fact, another equation (**eq. 2**) for capacitance can be formulated:

$$C = \frac{Q}{V} \qquad \textbf{eq. 2}$$

In **eq. 1** additional factors appear – ε_r and ε_0, which are the relative dielectric permittivity (also called a dielectric constant) and the vacuum permittivity ($8.85 \cdot 10^{-12}$ $F \cdot m^{-1}$), respectively. The relative dielectric permittivity is a dimensionless value; it describes a dielectric's ability to electric field establishment [14, 15]. As shown in **eq. 1**, the higher dielectric permittivity, the better. Capacitance of the capacitors widely used in small electronics is in the magnitude of picofarads (1 pF = 10^{-12} F).

It was mentioned that capacitors store energy. The energy stored in the electric field is defined as work (*W*) that is done by the external voltage source to fully charge the capacitor, i.e., to move electrons from one plate to the other, to a specific potential difference (ΔV, V). It can be described as follows:

$$W = q \cdot \Delta V \qquad \textbf{eq. 3}$$

However, taking into account voltage of the fully charged capacitor (*U*) and total charge transferred/stored, the energy stored (*E*, kWh) in the capacitor can be expressed by:

$$E = \frac{1}{2} Q \cdot U \qquad \textbf{eq. 4}$$

One would ask what does ½ mean? It comes from the fact that not all of the electrons come through maximum voltage (*U*) – only the first one needs to drop through this voltage. The next ones come through lower voltage. Keeping in mind that during discharge of the capacitor the charge stored gets lower, one can see that voltage also gets lower (**eq. 5**).

$$U = \frac{Q}{C} \qquad \textbf{eq. 5}$$

When combining the two former equations, the energy being dependent on capacitance is given:

$$E = \frac{1}{2} C \cdot U^2 \qquad \textbf{eq. 6}$$

In small electronics such capacitors can be sufficient. However, what if a device of higher energy is needed? To increase the amount of energy stored, electrochemical capacitors were constructed.

2.2. EC construction and the electrical double-layer model

In electrochemical capacitors porous carbon materials are used as electrodes (instead of metallic plates) which are in direct contact with current collectors (made of stainless steel, gold, titanium or another metal). The electrodes are separated by a membrane (a layer of polymer, glass, or paper) and everything is soaked in an electrolytic solution (**Fig. 2**) [12] (detailed description of electrode materials and electrolytes is provided in **section 2.3** and **2.4**).

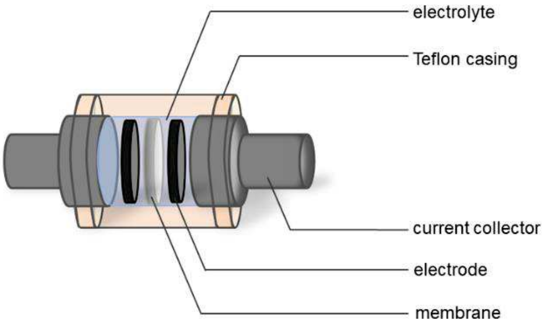


Fig. 2. Schematic representation of a laboratory-scale electrochemical capacitor

When the electrodes are immersed in the electrolyte, the movement of ions coming from the dissolved salt is observed – cations and anions spontaneously reach the electrodes surface [16, 17]. The mechanism of the energy storage in ECs is based on reversible charge accumulation at the electrodes' surface. Electrodes are polarized when the device is being charged – one has a positive charge and the second one has a negative charge; the ions start to arrange at the electrode/electrolyte interface creating an electrical double-layer (EDL). In years, a few models of EDL were described [18-20]. However, in the case of water-based ECs, where the double-layer is highly charged, the Stern model, which is the combination of previously described models, seems to be the most suitable [21]. Therein, the Stern model of EDL is discussed as an example of a positively charged electrode (**Fig. 3a**). Water molecules are attracted by the electrode surface with an oxygen atom oriented towards this surface. Moreover, the ions can be adsorbed specifically on the surface and the counter-ions can be adsorbed non-specifically onto it, removing part of the water molecules from surface [22]. This condensed molecules layer is called a stationary layer or a Stern layer. The electrode surface charge is partially neutralized by this layer, nonetheless a residual positive charge remains. Consequently, more anions, hydrated ones, are attracted by the electrode, and a second layer is developed. This layer is less ordered and more moveable than the Stern layer. It is called a diffuse layer or a Gouy-Chapman layer. Between the Stern and diffuse layers, the Stern plane is defined, passing through the nearest adsorbed hydrated anions. The distance between the electrode surface and the Stern plane is considered as an effective thickness of the double-layer and, in the case of carbon electrodes of the large specific surface area (SSA), is even lower than 1 nm. Taking a look at the electric potential changes (Φ) (**Fig. 3b**) at the electrode and the respective layers, one can notice, that a linear decrease of potential is seen at the Stern layer, dropping from the electrode potential (Φ_E). After exceeding the Stern plane, this drop is exponential and reaches Φ_b at the bulk of the electrolyte which is infinite far away from the electrode [12, 23, 24].

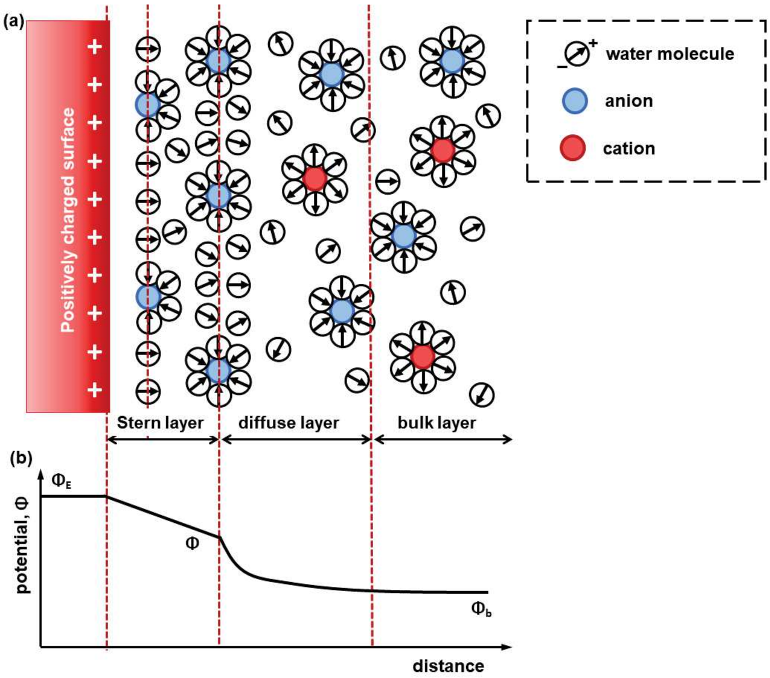


Fig. 3. (a) Stern model of EDL **(b)** with the electric potential changes [12]

Based on these assumptions, the electrode capacitance (C_E) can be calculated. It is considered as capacitance of two capacitors in series, giving:

$$\frac{1}{C_E} = \frac{1}{C_S} + \frac{1}{C_D}$$ **eq. 7**

where C_S – Stern layer's capacitance, C_D – diffusion layer's capacitance.

Electrochemical capacitors consist of two identical electrodes. That system is called the symmetric one. It can be presented by the equivalent circuit (**Fig. 4**). It is seen, that each electrode has its own capacitance ($C_{(+)}$ and $C_{(-)}$). Hence, the device "includes" two capacitors in series, so total capacitance (C) can be expressed as follows:

$$\frac{1}{C} = \frac{1}{C_{(+)}} + \frac{1}{C_{(-)}}$$ **eq. 8**

Assuming that both electrodes have the same capacitance ($C_{(+)} = C_{(-)} = C_E$), the **eq. 8** can be converted into:

$$\frac{1}{C} = \frac{1}{C_E} + \frac{1}{C_E}$$ **eq. 9**

$$\frac{1}{C} = \frac{2}{C_E}$$ **eq. 10**

$$C = \frac{1}{2} C_E$$ **eq. 11**

demonstrating, that capacitance of the device is twice smaller than capacitance of the single electrode. In these equations all capacitances should be expressed in Farads [9, 12].

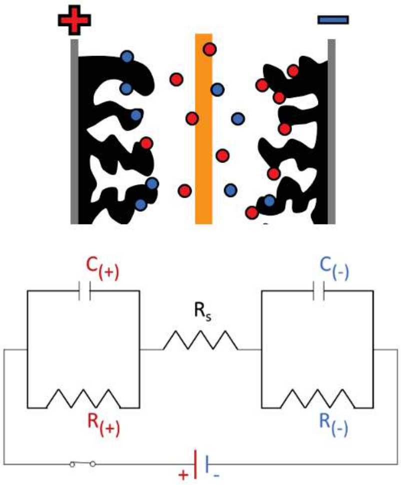


Fig. 4. Symmetric EC in a charge state scheme with its representation in form of the equivalent circuit [12]

In ECs various materials can be used as electrodes; their thickness and mass can also vary. In order to compare different devices' performance, such a characteristic value as capacitance should be recalculated per mass or surface of active material, giving gravimetric ($F \cdot g^{-1}$) or areal ($F \cdot cm^{-2}$) capacitance, respectively. Moreover, from an industrial point of view, size of a cell/device is crucial. Hence, the capacitance can be given per volume; then it is called volumetric capacitance ($F \cdot cm^{-3}$).

In the literature, the gravimetric capacitance is most often shown ($C_{/m}$). It is calculated by dividing the cell capacitance by the active mass of both electrodes (m_{act}).

$$C_{/m} = \frac{C}{m_{act}} \qquad \textbf{eq. 12}$$

However, the electrode capacitance is very often reported as well. Regarding the **eq. 11** and **eq. 12**, and the electrode mass ($0.5 \cdot m_{act}$) the gravimetric capacitance of the electrode ($C_{E/m}$) can be defined as:

$$C_{E/m} = \frac{C_E}{0.5 \cdot m_{act}} \qquad \textbf{eq. 13}$$

$$C_{E/m} = \frac{4 \cdot C}{m_{act}} \qquad \textbf{eq. 14}$$

$$C_{E/m} = 4 \cdot C_{/m} \qquad \textbf{eq. 15}$$

showing that for the symmetric system the gravimetric capacitance of one electrode is four times higher than the gravimetric capacitance of the cell. When compared the data from various scientific papers, one should take into account how the capacitance values were calculated.

In **Fig. 4** aside from two capacitors, resistors are marked (R_s, $R_{(+)}$ and $R_{(-)}$). Resistance in the system may arise from an electrode material and its electronic resistance, electrode/current collector and electrode/electrolyte interfaces, ions mobility in electrode porosity and an electrolyte itself but also from a separator. The cell resistance strongly impacts its performance. The sum of all the resistances existing between two current collectors is called the equivalent series resistance (*ESR*).

There are also other important parameters determining ECs' performance that allow different devices to be compared – the aforementioned energy (*E*) and power (*P*). Power of the device informs about the energy that can be delivered in a certain time. It can be calculated at the maximum operating voltage and 'corrected' by *ESR*:

$$P = \frac{U^2}{4 \cdot ESR} \qquad \textbf{eq. 16}$$

and as a function of the energy:

$$P = \frac{E}{t} \qquad \textbf{eq. 17}$$

where t stands for energy delivery time, i.e., for electrochemical capacitor discharge time [25, 26].

For comparative purposes providing these values per mass, area, or volume unit is recommended.

Moreover, self-discharge (SD) and leakage current (LC) are valuable parameters for the potential users of energy storage devices. SD is the cell voltage drop measured for the charged system at an open circuit, showing how the voltage decreases when the cell is not used. The higher SD, the worse, because it significantly affects the energy stored in the cell (according to **eq. 6**). The difference in free energy between the charged and discharged state of the EC is relatively high, therefore SD is also high – the system will aim at reaching the lowest possible energy [27, 28]. Moreover, because only electrostatic attractions occur at the electrode/electrolyte interface and porous electrodes are used (within which the solution resistance impacts the charge movement), SD in the ECs is relatively high in comparison with batteries [29]. Practical application of capacitors is strongly limited by high self-discharge. If the batteries are substituted for capacitors in the automotive industry, after a long time of non-using a vehicle, the EC voltage would be too low to start the engine. Therefore, ECs and batteries are very often used together. Then, the battery provides the charge to the EC to prevent its self-discharge. As a result, the battery is discharged faster, so more frequent charging is required [27]. SD of the ECs can be the result of possible parasitic Faradaic reactions [30, 31] and charge redistribution, i.e., the movement of charge within the electrode material, caused by the voltage difference between the fast polarizable surface of the electrode and its bulk [32-34]. The SD can be measured in a two-electrode setup where the real voltage drop of the device can be determined. It is also possible to employ the reference electrode to the tested cell and monitor the SD of each electrode separately. The result of such an experiment shows which electrode causes higher voltage loss and allows the mechanisms of SD for both electrodes to be determined [30].

If it is not possible to reduce SD, it is necessary to apply current to hold the voltage of the EC when the device is not used. Obviously, the lower this current, the better. Therefore, LC brings the information on what current is needed to stand by the cell voltage.

The comparison of various energy storage/conversion devices can be presented in a plot. It is so-called the Ragone plot, where the specific energy (Wh·kg^{-1}) is plotted *vs.* the specific power (W·kg^{-1}). Taking a look at **Fig. 5** where only a few selected examples of systems are presented, it is seen that electrochemical capacitors "fill the gap" between conventional capacitors (devices of tremendous power but very low energy) and battery technologies (with definitely higher energy but significantly lower power that are related to the oxidation and reduction reactions). Additionally, because of no faradaic reaction ongoing during charge and discharge of ECs, they are characterized by a long cycle-life [9].

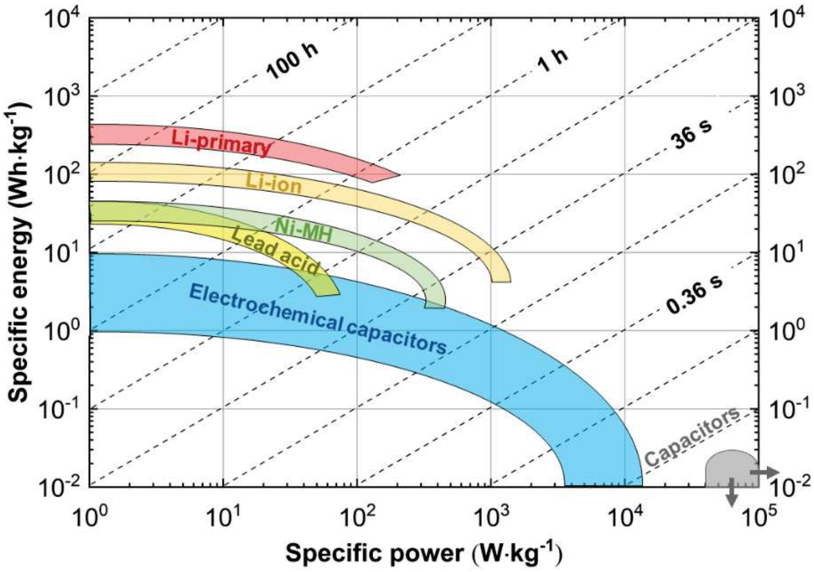


Fig. 5. The Ragone plot presenting the specific energy *vs.* the specific power for conventional capacitors, electrochemical capacitors and battery technologies (lead acid, nickel–metal hydride (Ni-MH), lithium-ion (Li-ion) and lithium primary batteries) [15, 35, 36]

The point is not to settle the matter of which device is the best, because it strongly depends on the prospective application. ECs can be used when a load needs energy pulses delivered in a very short time (even in milliseconds). They can be useful for small electronics of fluctuating loads (laptop computers, mobile phones, calculators, personal digital assistants, GPS) in order to power supply stabilization. However, ECs are also valuable in the automotive industry in electric and hybrid electric vehicles (merged with batteries) and aviation where they:

- provide cranking power even in very harsh conditions (at extremely low temperature),
- stabilize voltage in start/stop technology, especially for public transportation,
- store power during braking and release it assisting in a vehicle acceleration (it is called regenerative braking) and, in consequence, ease the burden on batteries prolonging their lifetime,
- serve as an emergency door opening systems in aircraft.

As already mentioned in the general introduction, electrochemical capacitors are used for the energy storage from installations based on renewable sources and also as buffers for grid stability improvement. Moreover, ECs ensure the safe operation of wind turbines, when wind speed is too high, by blade pitch adjustment or stopping the turbines [8, 10, 37-40].

There are many possibilities for electrochemical capacitor application in the energy industry. However, depending on the demanded parameters of the device, there is also a huge variety of available electrode materials and electrolytes, which need to be properly selected for EC construction.

2.3. Electrode materials for ECs

Requirements for materials used in electrochemical capacitors include high electronic conductivity and stability (especially in long-term performance and at elevated temperature), as well as high corrosion resistance. Moreover, a high specific surface area is necessary in order to accumulate large amount of charge. SSA of highly microporous samples and their composition are very often determined with nitrogen adsorption/desorption method (at 77 K) and calculated based on Brunauer-Emmett-Teller (BET) model [12].

Carbon materials are one of the most popular electrode materials, because of their diversity in structure and properties, which can be designed by applying different carbonization conditions and activation processes [9, 41, 42]. Materials applied in ECs can be characterized by various dimensionality, from 0D to 3D. A few examples of diverse materials will be listed and shortly discussed.

Onion-like carbons belong to the 0-dimensional group with varying carbon ordering within the shells. These materials provide the SSA about 500 $m^2 \cdot g^{-1}$ as an external, fully available surface [43]. Despite the satisfactory electrochemical performance, the cost of such a material is relatively high [44, 45]. Carbon nanotubes (CNTs) are among the 1-dimensional materials. They are built of a cylindrical graphene layer/layers; hence single- and multi-walled carbon nanotubes can be distinguished. They exhibit characteristic construction with a very high length/diameter ratio. Because of advanced synthesis methods, the cost of CNTs is quite high. CNTs themselves are characterized by moderate capacitance, therefore they are very often used as additives to the electrode materials, playing a role of a conductivity-increasing factor [46, 47]. Graphene is a 2-dimensional material, consisting of atoms monolayer, hence, its thickness is nearly equal to one atom. Graphene is characterized by a large surface area (about 2 600 $m^2 \cdot g^{-1}$, however, it is considered as an overestimated value, due to multiple edges in graphene), high electrical conductivity and good chemical/mechanical stability, giving the theoretical capacitance above 500 $F \cdot g^{-1}$ [48, 49]. Because of the graphene synthesis method, which demands strong oxidants, the final product is very often "contaminated" by oxygen. Another drawback of graphene is its tendency to agglomerate, producing graphite, and the capacitance of the material significantly decreases – down to about 100 $F \cdot g^{-1}$ in aqueous media [50]; such a capacitance value can be easily reached with the electrodes manufactured of cheaper and more available carbon materials. The last group – 3-dimensional materials, includes activated carbons, carbide-derived carbons and templated carbons.

Activated carbons (ACs) are the most common and in-depth investigated materials for EC application. Tremendous attention is given to ACs because of their extremely developed surface area – from 500 up to 3 000 $m^2 \cdot g^{-1}$, well-established manufacture procedure, availability and moderate cost of a final product. Moreover, they can be found in many different forms (powders, cloths, or foams) that made them useful at various applications [47, 51-53]. High SSA of ACs is the result of the pore network presence within the material. Pores, based on their size, are divided into three main groups: micropores, with a diameter < 2 nm, mesopores, with pores in the range 2 – 50 nm, and macropores, with a diameter > 50 nm. Moreover, supermicropores (> 0.7 nm) and ultramicropores (< 0.7 nm) were defined as the subgroup of micropores [54]. Macro- and mesopores are important for charge storage mechanisms, simplifying ion fluxes movement and their diffusion within the electrode; nonetheless, micropores are responsible for the very high capacitance of ACs. Carbon materials of high SSA are prepared through solid-state carbonization of a carbon-rich precursor. This process involves high temperature treatment (> 2 000°C) of the precursor in inert conditions. Depending on the carbonization temperature and time, structures of different morphology can be produced – highly porous carbons (in the case of the rapid process) and "glass-like" carbons of closed pores (when carbonization is performed long enough) [9, 25, 55, 56]. SSA, pore sizes and their distribution in the material strongly depend on the carbonaceous precursor used as well as the material activation method. Precursors for AC preparation can be both synthetic (polymers) or natural (pitches, cokes, wood, fruit and nutshells, seaweeds, or even flowers). However, a precursor should ensure high carbonization yield and its price should be possibly low. Because of the environmental issues and sustainable development of EC, natural precursors are favorable. One of the most popular precursors for AC synthesis is a coconut shell [57, 58]. As already mentioned, carbonized precursor can be activated, giving the material with the pores in nanoscale. Two types of activation processes can be distinguished. In the first one, called the physical activation, the material is oxidized (very often at a temperature in the range 700 – 1 100°C) using oxygen, air, steam, carbon dioxide, or a mixture of these gases, whereas H_2O steam and CO_2 are the most commonly used and the reactions are presented below [9, 25, 59, 60]:

$$C + H_2O \rightarrow CO + H_2 \qquad \textbf{eq. 18}$$

$$C + CO_2 \rightarrow 2CO \qquad \textbf{eq. 19}$$

The second activation procedure bases on using chemical agents like salt ($ZnCl_2$, $MgCl_2$, K_2S) as well as strongly alkaline (KOH) and acidic (H_3PO_4, H_2SO_4) solutions. Moreover, the chemical activation is very often carried out at an elevated temperature (up to 600°C), hence, the carbonization process before the activation is not necessary [61-64]. The chemical activation leads to the material of better-developed surface area production than the physical activation [65-68]. However, the SSA of the electrode material determined with the BET method cannot be directly translated into the capacitance of the EC. To get more precise information on the material texture, other models should be considered for the AC characterization (e.g., density functional theory, DFT, used for SSA estimation). Moreover, the pore size distribution (PSD) can be also determined, as an important parameter influencing the electrochemical performance of the EC [56]. Very high SSA is the consequence of a large contribution of micropores. For microporous material characterization it would be useful to apply not only N_2 as an adsorptive but also CO_2, because of hindered N_2 penetration into the narrow pores at low experiment temperature; higher CO_2 adsorption/desorption measurement temperature allows the gas molecules to enter the porosity, even into very narrow pores, due to the high enough energy of the CO_2 molecule [69]. The size and shape of pores are also important in terms of EC's capacitance. Electrode material porosity should be properly matched to the ion of electrolyte solution sizes. The diameter of the pores should be bigger/approximately equal to the ion diameters. In the case of slightly smaller pores, compared to the ion sizes, their penetration by anions and cations is still possible, if the ions lose their solvation shell or their structure is deformed. As these processes are quite complex and strongly depend on electrode material and electrolyte used but also on the experiment conditions, this topic is comprehensively studied in **section 3**.

Apart from ACs, carbide-derived carbons (CDCs) are porous materials with high SSA useful for ECs application. Their porosity can be controlled during synthesis, because of metal/metalloid extraction from carbide precursor at elevated temperature. The most promising electrodes for ECs, with narrow pore size distribution, are produced by the halogenation process. As the precursors, various carbides of silicon, titanium, molybdenum, or vanadium are very often used [70, 71]. Other interesting carbons for electrodes manufacture are templated carbons. Morphology and size of templated carbons' pores can be strictly controlled due to properly selected templates for the material production [72, 73]. Soft, hard and salt templated methods can be distinguished, giving materials of diverse SSA and PSD [9, 74-76]. The cost of such materials was said to be higher than other available materials and their diversity was considered as limited [9]. However, recently it was published that the preparation of templated carbons can be performed as a one-pot synthesis and great performance of ECs can be reached when the template is appropriately matched to the ions present in the electrolytic solution [77].

Carbon black, besides the most popular AC, is an interesting electrode material for EC application. It is widely used as an additive to the AC-based electrode material, because of its very high conductivity (between 0.1 – 100 $S \cdot cm^{-1}$). Nonetheless, carbon blacks characterized by high SSA (up to 1 800 $cm^{2} \cdot g^{-1}$) can be used as self-standing electrodes as well. They consist of colloidal size-carbon particles of near-spherical form that make them different from the previously discussed materials. Another important and unique feature of carbon black is the external porosity, easily available for ion adsorption, due to mesopores of wide size distribution making voids for ionic fluxes within the material. Additionally, the surface of carbon black contains a small number of functional groups, if any, that limits the unwanted side reactions, especially at elevated voltages [9, 25, 78].

In order to summarize properties of the above-mentioned electrode materials commonly used in ECs, as well as the possible capacitance of the devices operating in various electrolytes (aqueous, organic, or ionic liquids), the data were depicted as **Fig. 6** [9, 79].

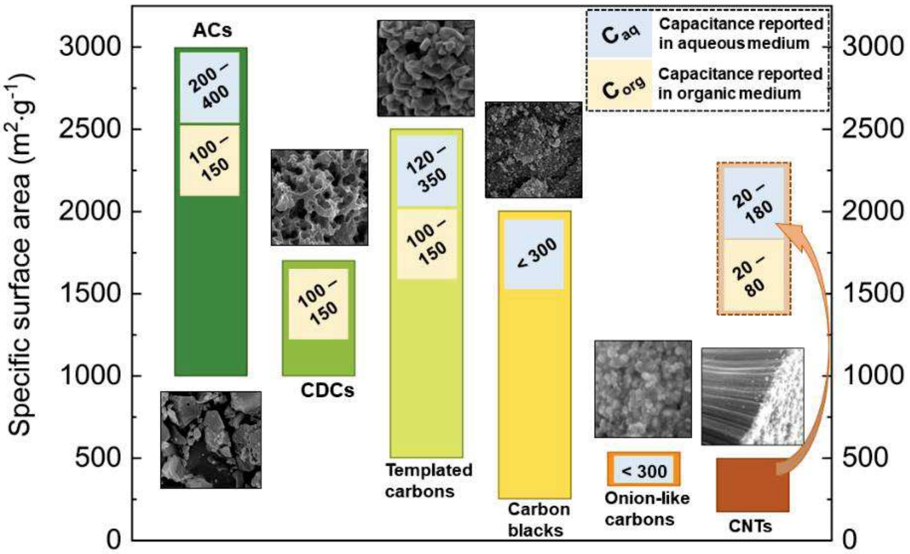


Fig. 6. Specific surface area and scanning electron microscope images of different popular electrode materials for ECs application with capacitance values reached when they are used in the system [57, 80-83]

2.4. Electrolytes for electrochemical capacitors

Electrochemical capacitors, but also other energy storage devices (mentioned on the Ragone plot, **Fig. 5**), need a conductive medium, called an electrolyte, being a source of ions that transport charges during EC operation, but also playing the role of an insulator between the electrodes. Electrolytes for ECs are the most often liquid [12, 84-90], however, they can also be in solid or semi-solid phase [84, 91-95]; the choice of the electrolyte-type strongly depends on the potential application – solid-state electrolytes are useful especially for wearable electronic devices [11, 96]. This work focuses on electrolytes in the liquid phase.

The electrolytic solution should meet specific requirements to be appropriate for EC including high ionic conductivity (in order to ensure EDL formation and, in consequence, electrodes' charge balancing during EC operation), wide electrochemical window (directly influencing the device's energy according to **eq. 6**) and stability at lowered/elevated temperature. From the practical point of view, the cost of such an electrolyte (at high purity) should be relatively low. Moreover, due to ecological issues and sustainable development of energy storage devices, an electrolyte should be low volatile and environmentally friendly [12, 84, 87]. When the necessary properties of electrolytic solution are defined, the suitable one can be found within one of three groups, which are: aqueous or organic electrolytes, or ionic liquids.

2.4.1. Aqueous electrolytes

Aqueous solutions are considered inexpensive and eco-friendly electrolytes. Moreover, they can be handled at ambient conditions, thus, EC assembling is simplified in comparison to organic electrolytes and ionic liquids. The operating voltage of aqueous-based cells is limited by water decomposition, occurring (theoretically) at 1.23 V [97]. Taking into account how strongly the energy depends on this parameter (based on **eq. 6**) limited voltage is a main drawback of aqueous electrolytes. On the other hand, aqueous solutions are characterized by high conductivity (up to 1 $S \cdot cm^{-1}$) and their application in ECs allows high capacitance (~180 $F \cdot g^{-1}$) and high power performance of the device to be reached [12, 98].

Aqueous electrolytes can be divided into acidic, alkaline and neutral solutions. The most popular acidic electrolyte is H_2SO_4 solution because of its high conductivity (e.g. 800 and 400 $mS \cdot cm^{-1}$ for 4 and 1 $mol \cdot L^{-1}$ H_2SO_4, respectively); capacitance values reported for AC-based ECs with such an electrolyte were between 100 – 300 $F \cdot g^{-1}$ (depending on the experimental conditions) [64, 99-103]. In the case of alkaline electrolytes, KOH solution is frequently used in EC application [12, 104]. The performance of the devices assembled with alkaline electrolytes is comparable to the reported for acidic electrolytes (due to large ionic conductivity, related to the outstanding OH^- and H^+ mobility) [14, 105, 106]. Nonetheless, the extremely low/high pH value of acidic/alkaline solutions boosts corrosion processes of the current collectors; hence, it is very often necessary to use more expensive and precious metals (like nickel or gold). Moreover, the practical maximum operating voltage for such systems was reported to be lower than 1 V, due to low hydrogen and oxygen evolution potentials, for acidic and basic medium, respectively. A narrow electrochemical window strongly limits the EC energy and the potential application of the device [104, 107].

The electrochemical stability of aqueous electrolytes is definitely higher when the solutions' pH is neutral (in the range from 6 to 8). Alkali metal salts solutions of sulfates, nitrates and chlorates are commonly used as electrolytic solutions in ECs. Depending on the current collectors' type, the maximum operating voltage significantly exceeds the theoretical voltage of water decomposition. In the case of Na_2SO_4 solution, EC safe operating voltage of 1.6 V was reported [108-110]; when Li_2SO_4 solution was used for the device construction, this parameter considerably increases – up to 2.2 V in 1 $mol \cdot L^{-1}$ salt concentration at gold current collectors [85]. Reaching such a high voltage is possible, because of overpotentials of hydrogen and oxygen evolution potentials (related to local pH changes near electrodes during the cell operation) and the positive impact of the solvation shell of ions, which is the highest at neutral pH [85, 97, 111]. The capacitance of "neutral-based ECs" is lower than recorded in both alkaline and acidic medium (~120 – 180 $F \cdot g^{-1}$), however, they ensure safer operating conditions, wider electrochemical stability widow and give the possibility of using cost-effective stainless steel current collectors [85, 112-117].

2.4.2. Organic electrolytes

Commercially, ECs based on organic electrolytes are commonly used. They consist of salt, the most popular is tetraethylammonium tetrafluoroborate ($TEABF_4$), but also lithium or sodium hexafluorophosphate ($LiPF_6$, $NaPF_6$), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium perchlorate ($LiClO_4$), dissolved in an organic solvent – e.g., acetonitrile (ACN), propylene carbonate (PC), adiponitrile, dimethylsulfoxide and others. They offer higher maximum operating voltage than aqueous-based systems – even up to 3.7 V; typically, this voltage varies between 2.7 and 2.8 V. However, the specific capacitance is noticeably lower if compared with an aqueous medium (below 150 $F \cdot g^{-1}$) [12, 87, 118-123]. Despite the satisfactory performance of ECs operating in organic electrolytes, there are many issues mostly related to the properties of the chemicals used and the price of the final product. First of all, organic solvents are toxic, volatile and flammable and these properties allow them to be considered non-eco-friendly. Additionally, they have a negative impact on the safety of organic-based systems. Secondly, one should think about the water content in the electrolyte and its purity. Impurities and humidity will limit the operating voltage of the cells, due to unwanted redox reactions and water decomposition at elevated voltages. Hence, both the storage of the EC's components and the assembly of the cell should be done inside an inert atmosphere glove box. These facts make the process of the manufacturing of the systems more time-consuming and increase their cost [57, 124-126].

2.4.3. Ionic liquids

Ionic liquids (ILs) are liquid compounds composed entirely of ions (no solvent). A melting point below 100°C is very often defined for ILs [87, 127]. A cation of IL is, usually, organic (bulky and asymmetric), whereas an anion can be both organic and inorganic [128-130]. They are ionically conductive without the necessity of any solvent used. They are, in consequence, characterized by low vapor pressure [12, 122]. ILs are an alternative group of electrolytes for ECs – they are able to operate at a wide potential range but, unlike the organic electrolytes, they are called "green" and safe electrolytes [131-133]. Moreover, they have high thermal stability and the ILs-based EC can operate safely and efficiently even at very harsh conditions (at the temperature in the range from -50 up to +80°C) [133, 134].

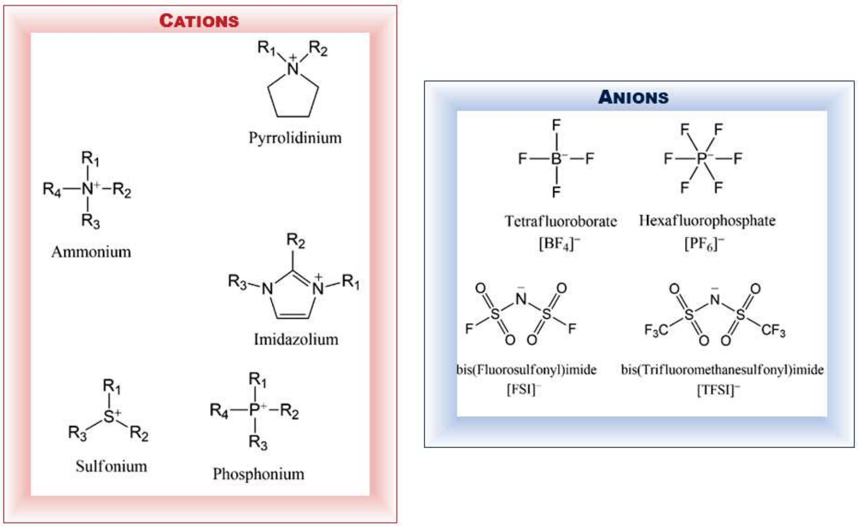


Fig. 7. The most popular cations and anions used in ILs

Generally, the physicochemical properties of ILs depend on the cation-anion combination, which can be considered unlimited due to the large variety of ions. ILs based on ammonium (including tetraalkylammonium, imidazolium and pyrrolidinium [16, 135-139]), phosphonium [140-142] and sulfonium [143-145] cations are the most popular for ECs application. In the case of anions, organic ones include e.g. dicyanamide (DCA^-) [146, 147], bis(trifluoromethanesulfonyl)imide ($TFSI^-$) [144, 148, 149], bis(fluorosulfonyl)imide (FSI^-) [134, 150-152] and as inorganic anions tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) are the most popular ones. The formulas of the mentioned ions are presented in **Fig. 7**. Bearing in mind the requirements for solutions for being used in EC, poor conductivity and high viscosity of ILs are their main disadvantages. If to compare the conductivity of ILs (for example 13.6 $mS \cdot cm^{-1}$ of 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIm^+][BF_4^-]$, as one of highly conductive IL [153]) with the conductivity of organic (50 $mS \cdot cm^{-1}$ of commonly used $TEABF_4$ in ACN [154]) and aqueous solutions (up to 100 $mS \cdot cm^{-1}$ of neutral sulfates salts [85]), these values are definitely lower. Such a poor conductivity and high viscosity impact the EC performance – due to higher resistance and reduced electrodes' wetting, the charge propagation and power rate can be limited [155, 156].

Synthesis of ILs can be generally performed in two steps. The first one leads to the formation of the required cation. The process includes an amine protonation (with an acid) or a quaternization reaction (by using haloalkane R'X at elevated temperature). However, this step can be very often skipped, because many cations in a halide form are commercially available. If at least one hydrogen is bonded to the central atom of the cation, the synthesized IL will be called protic. Otherwise, when alkyl or aryl groups are substituents of the central atom, an aprotic ionic liquid will be produced. The second step is the anion exchange reaction when the desired anion takes halide anion's place. Thus, the halide salt reacts with metal salt ($M^+[A]^-$), Brønsted acid ($H^+[A]^-$) or ion exchange resin giving a final product and a by-product. Such a reaction is called a metathesis reaction. The other possibility is a reaction of the halide salt with a Lewis acid (MX_y) [157-159]. As a popular Lewis acids for ILs preparation ethylaluminum dichloride ($C_2H_5AlCl_2$) [127], CuCl [160], BCl_3 [161] and $AlCl_3$ [157, 162-164]. The latter compound is the most commonly used. Described synthesis paths are presented schematically in **Fig. 8**. No matter the pathway of IL synthesis, this process can be performed in an ambient atmosphere. However, for ECs application, each non-aqueous electrolyte should be properly dried if the device is supposed to operate at a wide electrochemical window. Thus, the synthesized IL should be possibly clean (with no substrate residues) with water content below 20-50 ppm. Unfortunately, electrochemically and thermally stable green ILs are relatively expensive, which limits their practical utilization as electrolytes in the energy storage devices market [87, 165].

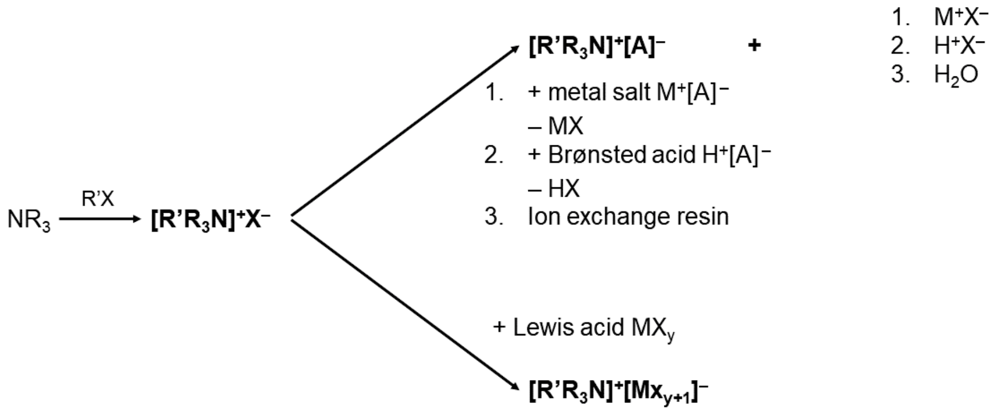


Fig. 8. Schematic representation of two-steps ILs synthesis [157]

2.5. Enhancement of ECs performance

2.5.1. Pseudocapacitive materials

It is well known that, despite many advantages, ECs suffer from limited energy in comparison with batteries. In order to enhance the energy density of these systems, the capacitance can be increased (according to **eq. 6**) by introducing redox-active materials [12]. In addition to electrical double-layer formation (**Fig. 9a**) the Faradaic reactions, involving the charge transfer at the electrode/electrolyte interface, are provided (**Fig. 9b**). This phenomenon is called pseudocapacitance. It is recommended to call EC with such a redox activity as an asymmetric device [166, 167].

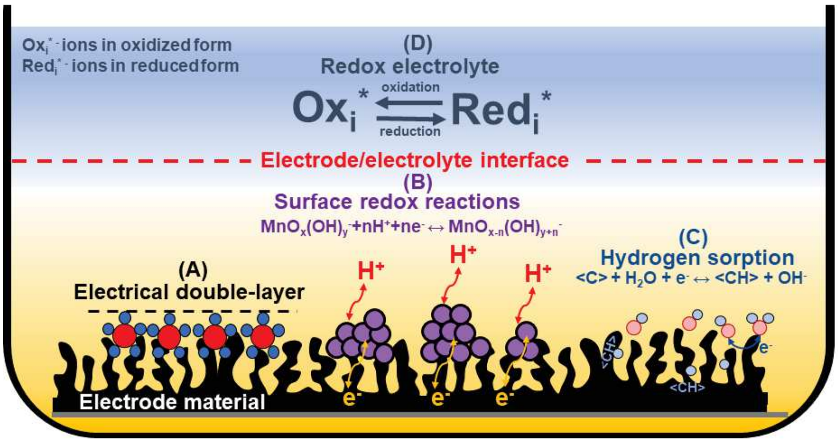


Fig. 9. Mechanisms of ECs charging based on **(a)** the electrical double-layer formation, **(b)** redox activity at electrode/electrolyte interface, originating from electrode material, **(c)** reversible hydrogen electrosorption in nanoporous material and **(d)** redox reactions coming from electroactive species from the electrolyte; based on [36, 168, 169]

The definition of pseudocapacitance has been extended within many years, with the development of new materials for ECs application [167, 170-173]. It is worth mentioning that there are many materials exhibiting redox activity, whereas, not all of them should be classified as pseudocapacitive ones. The term "pseudocapacitance" means that the electrochemical behavior of the electrode confusingly resembles EDL formation, observed as a constant current registered over the whole potential range and the calculated capacitance is the same at each point. However, the current flow's origin is different, i.e., it comes from the reversible redox reactions, ongoing very fast, with the charge flow through the double-layer. Comparison of different energy storage mechanisms is presented in form of voltammograms in **Fig. 10** [174], where an oxidation state changes in "pseudocapacitor" are indicated as dashed lines.

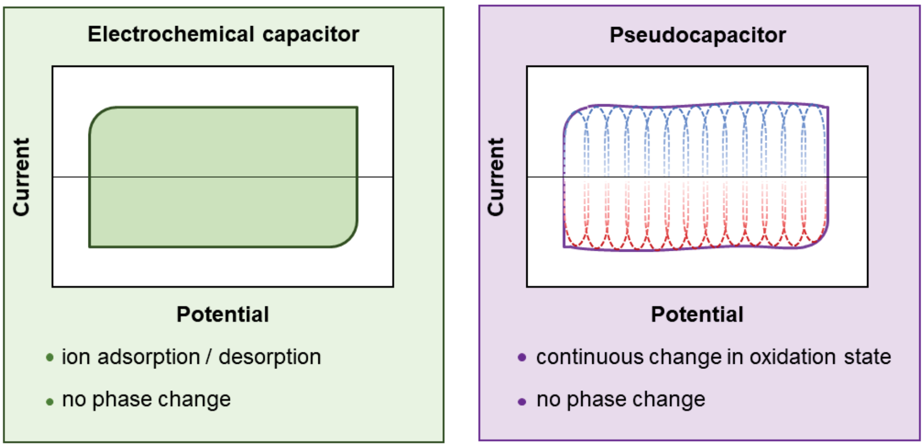
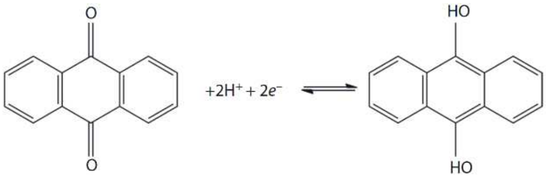


Fig. 10. Mechanism of energy storage in an electrochemical capacitor and a pseudocapacitor [174]

As a typical example of pseudocapacitive electrode material MnO_2 can be presented, where the Mn^{4+} is reduced to Mn^{3+} and the proton/cation insertion from the electrolytic solution occurs at the same time [167, 175]. In the case of the battery-type materials, like $Ni(OH)_2$ or PbO_2, it is impossible to calculate the average capacitance, hence the current is not constant (oxidation/reduction peaks are registered during cyclic voltammetry or a plateau is seen at a galvanostatic profile) at the considered potential window [176-178]. For that reason, such materials cannot be classified together with typical pseudocapacitive materials like MnO_2 [167].

If electrode materials are enriched with heteroatoms (oxygen and nitrogen), synthesized as composites based on conducting polymers (polyaniline, polypyrrole), incorporate transition metal oxides (i.e. RuO_2, MnO_2) or functional groups at the surface (like anthraquinone, AQ), they can be classed as pseudocapacitive materials [36, 179-184]. Electrochemical behavior of pseudocapacitive materials strongly depends on the electrolyte used; for example, an activated carbon modified with AQ groups exhibits redox activity in acidic pH, because a proton is needed for 1,4-benzoquinone (known as quinone) reduction to give benzene-1,4-diol (hydroquinone) **eq. 20** [84, 185]. The main drawbacks of pseudocapacitive material are their cost, which is higher than the cost of ACs, and unstable electrochemical behavior, especially during long-time operation. Moreover, the ions diffusion and electrode penetration are limited in the case of such modified materials [12, 56, 186].



eq. 20

2.5.2. Hydrogen electrosorption

Another way of EC's capacitance increase is the use of water electrodecomposition process in aqueous electrolytes, especially in strongly acidic and alkaline electrolytes (3 $mol\cdot L^{-1}$ H_2SO_4 and 3 $mol\cdot L^{-1}$ KOH [168]) but also in sulfate-based solutions with properly adjusted pH (presented schematically in **Fig. 9c**) [187]. During EC operation at the negatively polarized electrode, when the cathodic potential is lower than the equilibrium potential, hydrogen H is generated (according to **eq. 21** and **eq. 22** for the alkaline and acidic medium, respectively) and electrosorbed at the electrode surface ($<CH_{ad}>$) (**eq. 23**) with further diffusion into the material porosity.

$$H_2O + e^- \rightarrow H + OH^- \quad \textbf{eq. 21}$$

$$H_3O^+ + e^- \rightarrow H + H_2O \quad \textbf{eq. 22}$$

$$< C > + H_2O + e^- \rightarrow < CH_{ad} > + OH^- \quad \textbf{eq. 23}$$

This process is reversible, hence when the polarization is reversed, hydrogen is desorbed and then oxidized, forming water with OH^- anion presents in the electrolyte bulk [168].

2.5.3. Redox-active electrolytes

To enhance the energy of carbon-based ECs, the incorporation of redox-active electrolytes is a very popular approach (**Fig. 9d**). There are many electrolytes with well-defined redox couples, which could be useful in this matter. Chum *et al.* summarized them and arranged based on their standard reduction potentials (**Fig. 11**) [90, 97].

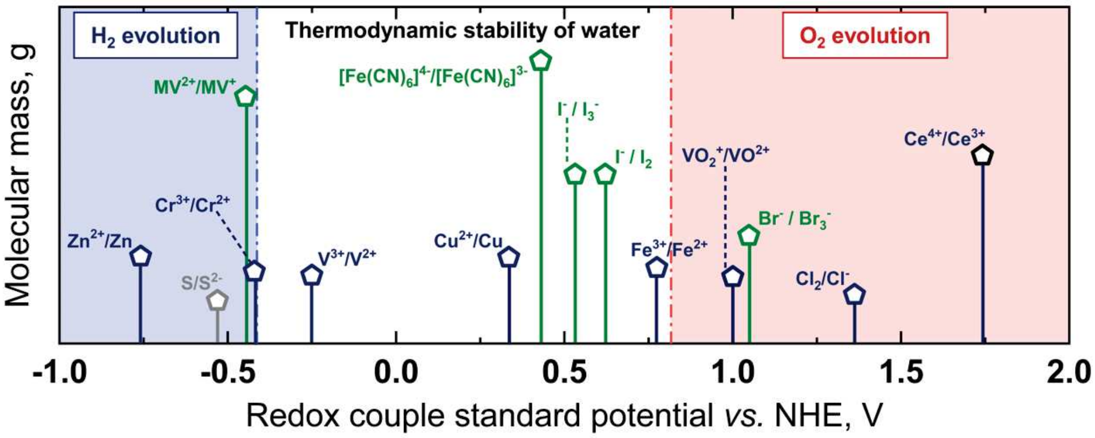


Fig. 11. Reduction potentials of redox couples (presented vs. normal hydrogen electrode, NHE), popular as electrolytes/additive to electrolytes in ECs application. MV stands for methyl viologen; H_2 and O_2 evolution regions and water thermodynamic stability are depicted as well; based on [90, 97]

The stability and activity of the redox couples strongly depend on the solution pH. There are couples stable at acidic, alkaline and neutral medium (marked as blue, grey and green symbols, respectively). The choice of appropriate redox couple should be done based on preliminary assumptions, regarding the cell design (electrolyte pH, electrode material, current collectors type) and potential application of the system. The activity of redox pairs is seen in electrochemical tests as a sharp current increase at specific potential (just like in the case of batteries). An exemplary voltammetry profile for typical reversible redox response during the cell polarization is presented in **Fig. 12** [174].

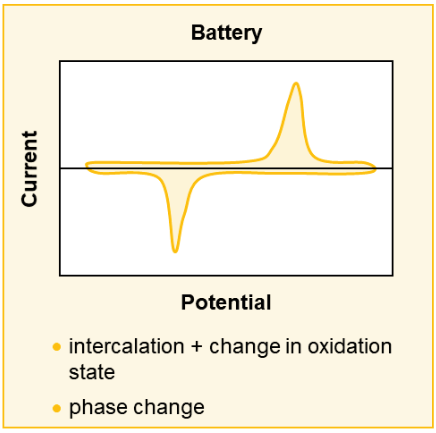


Fig. 12. Cyclic voltammogram recorded typically for batteries, where well-defined redox current increase is seen [174]

Both aqueous and non-aqueous solutions of halides – bromides [90, 188, 189] and iodides [190-197] are common electrolytes, exhibiting redox activity, widely studied over the last decade [198-202]. Because of the lower standard potential of iodide/iodine redox couple, if compared with bromide/bromine potential (0.62 vs 1.08 V *vs.* NHE, respectively [97]), corrosion phenomenon observed when bromide-based electrolytes are used, safety and environmental friendliness, iodide salts solutions seem to be more convenient for EC applications [193].

The redox activity of iodides is mostly related to the following reaction, i.e., iodide I^- oxidation to iodine I_2 [97, 190]:

$$2I^- \leftrightarrow I_2 + 2e^- \qquad \textbf{eq. 24}$$

However, there are also other possible reactions, presented in form of a potential-pH equilibrium diagram, so-called the Pourbaix diagram (**Fig. 13**). When iodine I_2 is dissolved in the solution and reacts with I^-, they recombine into polyiodides complex I_3^- (**eq. 25**). In the Pourbaix diagram this reaction is presented as **eq. 26** and **eq. 27**. During long-time operation another complex can be formed (I_5^-) according to **eq. 28**. The occurrence of these forms of (poly)iodides was confirmed with Raman spectroscopy [193]. Moreover, depending on the electrolyte pH, iodate ion IO_3^- can be formed as well (**eq. 29** and **eq. 30**).

$$I^- + I_2 \leftrightarrow I_3^- \qquad \textbf{eq. 25}$$

$$3I^- \leftrightarrow I_3^- + 2e^- \qquad \textbf{eq. 26}$$

$$2I_3^- \leftrightarrow 3I_2 + 2e^- \qquad \textbf{eq. 27}$$

$$I_3^- + I_2 \leftrightarrow I_5^- \qquad \textbf{eq. 28}$$

$$I_2 + 6H_2O \leftrightarrow 2IO_3^- + 12H^+ + 10e^- \qquad \textbf{eq. 29}$$

$$I^- + 3H_2O \leftrightarrow IO_3^- + 6H^+ + 6e^- \qquad \textbf{eq. 30}$$

If looking at the Pourbaix diagram other forms of iodine-containing compounds are also possible. However, from a practical point of view, in electrochemical systems their existence is rather doubtful. Redox reactions into compounds of a higher iodine oxidation state require a very high potential, much higher than the oxygen evolution potential, hence the electrolyte decomposition and electrode material oxidation would be seen at such harsh conditions.

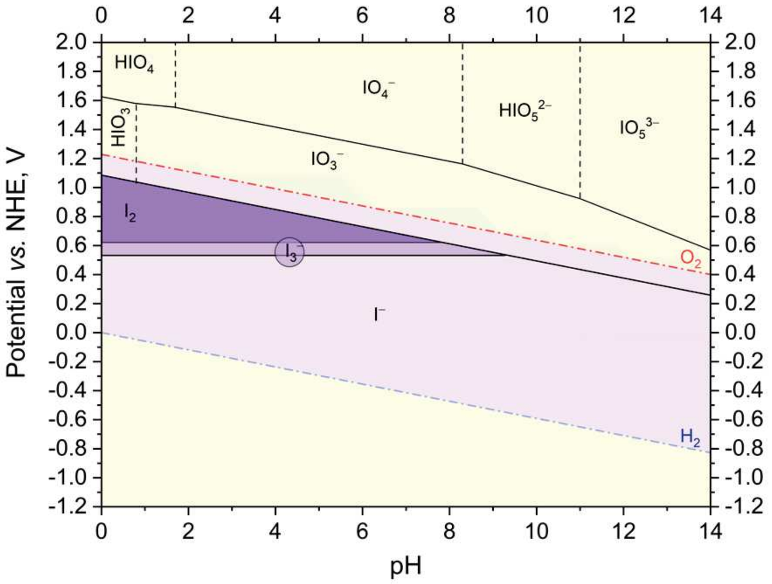


Fig. 13. Pourbaix diagram for iodine/water-based system, calculated for 1 mol·L^{-1} solution at 25°C [97]

In EC, the reactions of iodides are observed as a rapid current increase at the electrode polarized positively, which operates at the very narrow potential range, whereas the negative electrode exhibits mechanism typical for ECs (charge is accumulated electrostatically at the electrode surface) (**Fig. 14**) [190].

The systems with redox-active electrolytes generally suffer from shorter cycle-life in comparison with typical EC (with pure electrostatic charge accumulation) [203]. However, it has been shown, that the additive of iodides to the neutral sulfate-based electrolyte reduces self-discharge of the device and relatively high cell voltage can be successfully applied (1.6 V) [204].

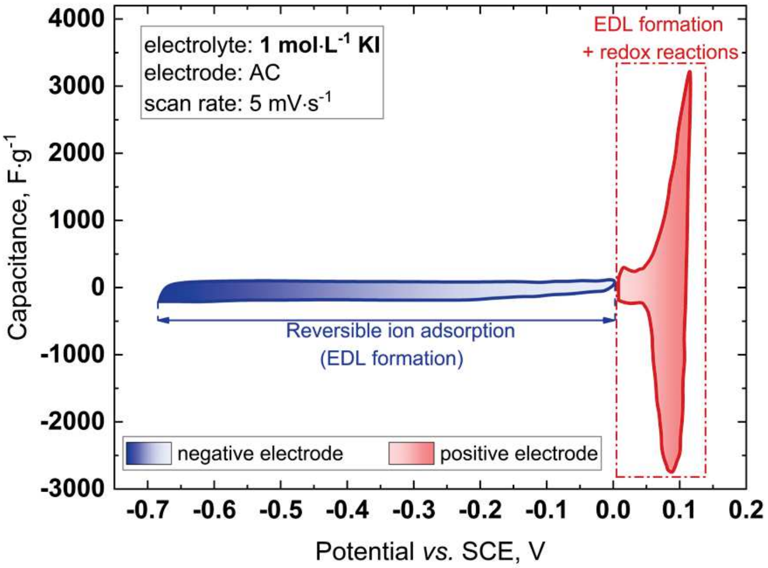


Fig. 14. Voltammogram profiles recorded for each electrode separately, recalculated to capacitance in the function of applied potential [190]

It is seen, that electrolytes with redox-active species are promising solution for ECs' performance enhancement. However, it seems that the potential of these electrolytes has not been fully achieved so far.

3. Fundamental studies of the charge storage mechanism in ECs

Electrochemical capacitors cannot be classified as new devices – they were commercialized in the second half of the 20th century by Nippon Electric Corporation. However, in order to improve ECs' performance, it is crucial to understand and properly describe the energy storage mechanism within these devices. Some basic information of the EDL formation at the electrode/electrolyte interface can be got from simple electrochemical tests. However, advanced techniques are necessary for such extensive studies. *In-situ* tests are powerful for ECs investigation and they are performed during the cell's operation. Additionally, *post-mortem* analyses are useful, mainly defining the reasons for capacitor performance fading and cycle-life shortening, since they are done when the cell reaches its *end-of-life* criterion.

Various techniques can be applied for fundamental studies of EDL formation mechanism and the device's aging process, i.e.:

- spectroscopy techniques (like Raman, infrared and nuclear magnetic resonance (NMR) spectroscopy),
- scanning probe microscopy techniques (atomic force microscopy, scanning electrochemical microscopy (SECM)),
- electrochemical quartz crystal microbalance (EQCM),
- electrochemical dilatometry (ECD),
- nitrogen adsorption/desorption.

Each technique gives the specific information of the ongoing processes, therefore, to get a complete picture of the investigated phenomenon is it very often necessary to use more than one technique.

For example, EQCM experiments allow the movement of the ions to the electrode surface to be monitored during the cell operation. However, no information concerning the ions' presence or their movement within the material porosity can be gained [205]. Raman spectroscopy can be used to describe the changes in the carbon electrode's structure since it is sensitive to the carbon-carbon bonds (as they are symmetric covalent bonds) [92, 206]. Raman spectra of the electrodes can be done before, during, and after electrochemical tests, and then compared; in such a case they are performed as *ex-situ* experiments. It is also possible to collect the spectra during the electrochemical investigation and observe the structural changes at different potentials applied. Moreover, if there are new bonds created between the material and species from the electrolyte or a precipitate is formed, additional peaks can be seen in the Raman spectrum. In order to look deeper into the electrode porosity, an NMR spectroscopy can be used. It allows both cations and anions within the pores to be recognized but also quantified [16, 207]. Volumetric change of the electrode during the EC operation can be measured with an ECD as well as with a SECM. In the ECD the changes in height of the investigated electrode are directly registered by the micrometer screw. In the case of the SECM, the current flows through an ultramicroelectrode (a tip) close to the conductive carbon material. The ultramicroelectrode scans the material in *x* and *y* directions, and the electron transfer reaction at the tip or the substrate surface under the tip is monitored. As a result, the map of the electrode's surface can be drawn providing an information about surface topography [208].

As already mentioned, nitrogen adsorption/desorption can be used for a freshly prepared electrode material characterization but it is also helpful for *post-mortem* analyses, showing the difference in SSA and pores' size and distribution before and after the electrochemical tests.

Fundamental studies on ionic fluxes and the EDL formation focus on ionic liquids and organic electrolytes. The assumptions concerning these processes are schematically presented in **Fig. 15**. Just after the electrode is immersed in the electrolytic solution spontaneous ions movement to the electrode surface and pores filling are detected (**Fig. 15a**). When the cell is being charged, the counter-ions are attracted to the electrode's surface and penetrate its pores for the negatively polarized electrode (**Fig. 15b**). At the same time for the electrode polarized positively, first mainly co-ions are expelled from the material porosity (**Fig. 15c**). Then, at high enough potential (depending on the electrolyte composition, ions' size, a solvent used and material's porosity) counter-ions adsorption is believed to mainly be responsible for balancing the electrode's charge, however, still, co-ion desorption was confirmed (**Fig. 15d**) [16, 200, 209-211]. Nonetheless, the processes of charge storage at the electrode/electrolyte interface are still ambiguous. It is not clearly defined how ions size, their mass and electrode material type impact the EC charging process. In the case of ILs it is possible to study the effect of ion size on the EDL formation (because of lack of solvent molecules). For aqueous electrolytes solvation shell needs to be taken into consideration, therefore the influence of the electrolyte's pH would be interesting to investigate.

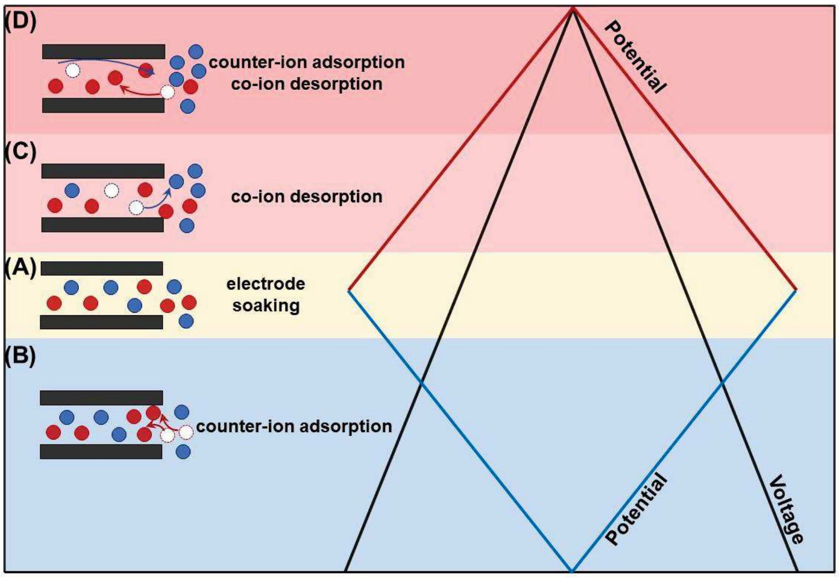


Fig. 15. Schematic picture of the ions movement at the surface and within the porosity of the electrode material immersed in the electrolyte **(a)** and during the EC charging – for the electrode polarized negatively **(b)** and positively **(c, d)**

THE AIM OF THE WORK

Electrical double-layer capacitors are recognized as being highly-power, but relatively low-energetic devices. Therefore, **the aim of this work is the electrochemical capacitors performance improvement**.

Redox reactions ongoing during the EC charge/discharge allow higher charge to be accumulated at the electrode, thereby allowing to reach higher capacity of the system. As already presented in **eq. 6**, capacitance increase directly impacts the energy of the device. Since the similarities between halides and pseudohalides are mentioned in the literature, it was the motivation to attempt to use pseudohalide solutions as electrolytes in ECs. Moreover, they were used in solar cells, where their redox response was well-defined and stable in time. Considering the above, **the research hypothesis arises – pseudohalide solutions can be used as electrolytes for electrochemical capacitors and effectively increase their capacitance and, in consequence, the specific energy**. The effect of the electrode material, the redox-active species concentration, the type of electrolytic medium, and nanoparticle addition were investigated.

Herein, aqueous solutions of thiocyanate and selenocyanate-based salts are utilized as electrolytes for ECs. Moreover, ionic liquid with selenocyanate anion is synthesized and also used as the electrolyte (**Chapter II**). ECs are assembled with widely used activated carbon electrodes. All the components are eco-friendly because, nowadays, it is very important to take into consideration the environmental issues while designing new devices.

The processes ongoing during EC charging/discharging and mechanism of charge storage should be also elucidated in the frame of fundamental research. However, the results of these studies can have practical meaning and, by extension, be valuable in the further development of energy storage devices. Therefore, in **Chapter III** the ionic fluxes and mechanism of charge accumulation near/within the polarized electrode are described based on the electrochemical dilatometry studies. The differences between the behavior of the electrodes in different electrolytes (ionic liquid and aqueous solutions) are presented. Moreover, the effect of the electrode material's type is verified for IL as the electrolyte. In the case of aqueous electrolytes, the influence of the pH value of the solution on the charge storage mechanism was studied.

CHAPTER II

Redox-active electrolytes in electrochemical capacitor application

Four publications attached:

P1. Górska B., Bujewska P., Fic K., *Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors*, Physical Chemistry Chemical Physics 19 (2017) 7923-7935

P2. Bujewska P., Górska B., Fic K., *Gold nanoparticles for power retention in electrochemical capacitors with KSCN-based aqueous electrolytes*, Journal of Power Sources Advances 14 (2022) 100087

P3. Bujewska P., Górska B., Fic K., *Redox activity of selenocyanate anion in electrochemical capacitor application*, Synthetic Metals 253 (2019) 62-72

P4. Fic K., Górska B., Bujewska P., Béguin F., Frąckowiak E., *Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors*, Electrochimica Acta 314 (2019) 1-8

Summary of the publications

As already mentioned in **Chapter I**, ECs suffer from moderate specific energy (between 1 and 10 Wh·kg^{-1}), whereas their power rate is tremendous if compare to other popular energy storage devices (even 10^4 W·kg^{-1} *vs.* $10^2 - 10^3$ W·kg^{-1}) (**Fig. 5**) [12, 15].

In order to improve the performance of ECs, where only EDL is formed during the device charging, the utilization of redox-active electrolytes can be considered. Herein, in **Chapter II**, the summary of the studies on new promising electrolytes for ECs' application is presented. Since halide-based solutions containing iodide/iodine or bromide /bromine redox couple were successfully employed in ECs, an application of pseudohalide solutions was proposed.

First of all, alkali metal and ammonium thiocyanate solutions were investigated within the paper **P1** entitled *Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors*. Thiocyanate anion activity can be presented as similar to iodide activity. First, the anion is adsorbed (**eq. 31)** and oxidized (**eq. 32**) on the positively polarized electrode. Then, a dimer is formed: $2SCN^- / (SCN)_2$. Going further, the polymerization reaction is possible as well (**eq. 33**).

$$SCN^-{}_{(bulk)} \rightarrow SCN^-{}_{(ads)} \quad \textbf{eq. 31}$$

$$SCN^-{}_{(ads)} \rightarrow SCN^\bullet{}_{(ads)} + e^- \quad \textbf{eq. 32}$$

$$xSCN^\bullet{}_{(ads)} \rightarrow (SCN)_{x(ads)}. \quad \textbf{eq. 33}$$

These processes have been described as reversible ones, which makes them commonly used in photoelectrochemical cells [212]. In the frame of this paper, aqueous thiocyanate-based electrolytes of four different cations (K^+, Na^+, Li^+ and NH_4^+) and various concentrations were tested as electrolytes for EC.

These solutions are characterized by high solubility and very high conductivity values (especially KSCN and NH_4SCN solutions, **Fig. P1.1**) – significantly higher than the conductivity of neutral sulfate-based electrolyte (saturated K_2SO_4 – 99 mS·cm^{-1}, 1 mol·L^{-1} Li_2SO_4 – 75 mS·cm^{-1}). Moreover, the impact of current collectors on the cell's electrochemical behavior was studied.

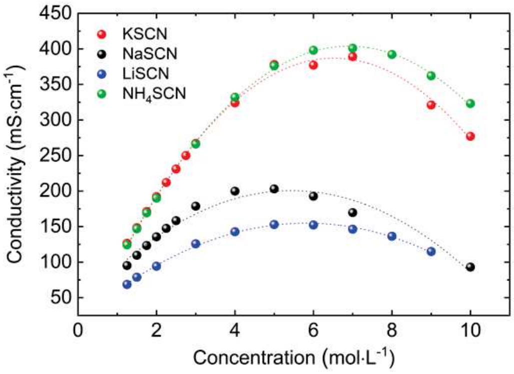


Fig. P1.1. Conductivity of the thiocyanate-based salt solutions measured in various concentrations (from 1 up to 10 mol·L^{-1})

Three different materials – stainless steel, gold and titanium, at various conditions were tested. In the case of slow/moderate scan rates applied, the differences of the systems' behavior were negligible. However, when a relatively fast scan rate was used (200 mV·s^{-1}) the redox response was definitely better pronounced and the charge propagation was improved (**Fig. P1.2**). Nonetheless, for further studies, current collectors of stainless steel were selected, because of economic issues.

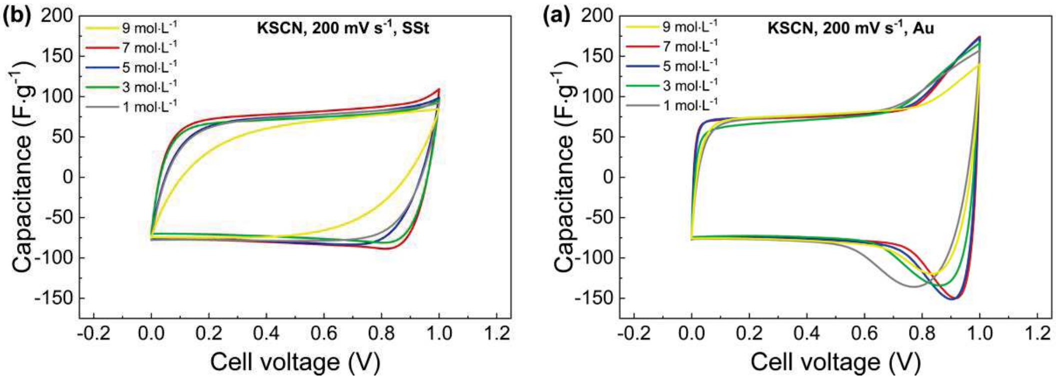


Fig. P1.2. Capacitance, calculated per one electrode' mass, in the function of applied voltage for the systems operating in KSCN-based electrolytes of various concentrations at **(a)** gold and **(b)** stainless steel current collectors

It has been found that each of the tested solutions can be applied as a redox-active electrolyte in EC, reaching a relatively wide voltage window – up to 1.6 V (water decomposition voltage is notably exceeded). However, the electrode material type strongly affects the device's performance – the best energy/power characteristic was observed for micro/mesoporous carbon. Depending on the cation, different maximum cell voltages were determined, hence the cycle-life also varied between 10 000 up to 100 000 cycles (at the same current density applied). Hence, one of the proposed solutions can be selected after determining the required parameters and potential application. Due to looking for environmentally-friendly components for ECs, it was also important to find out whether some toxic compounds are produced during long-term experiments. With Raman spectroscopy, performed in *operando* mode, neither cyano-groups nor hydrogen cyanide (CN^-, HCN, respectively) was detected (stretching vibrations of the C≡N bond are expected to be seen at 2050 cm^{-1} Raman shift) (**Fig. P1.3**).

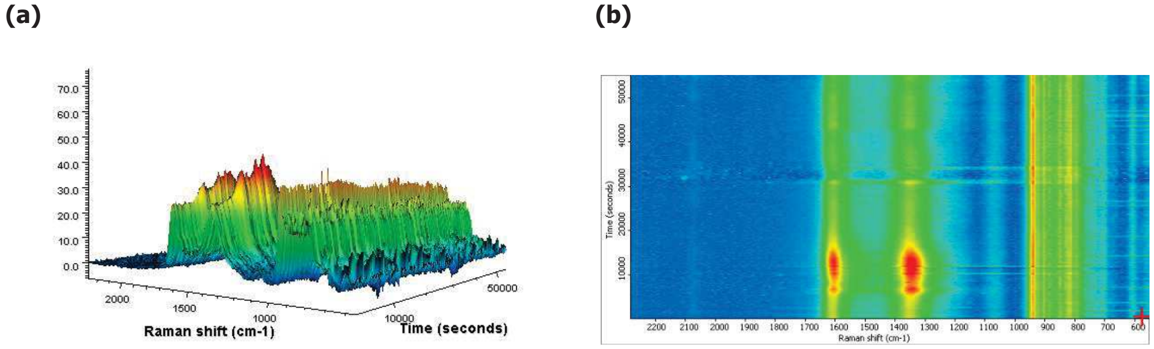


Fig. P1.3. *Operando* Raman spectra of the polarized electrode recorded at the time of the experiment, presented as **(a)** the 3D colormap and **(b)** the 2D map

Noticing the positive impact of gold current collectors on the performance of EC operating in thiocyanate salt-based electrolyte, the idea of adding gold nanoparticles (AuNPs) into the electrolytic solution arose. Gold was chosen because of known interaction between this metal and thiocyanate anion [213] and the insolubility of gold in such a solution. The results of this work were described in the paper **P2** entitled "*Gold nanoparticles for power retention in electrochemical capacitors with KSCN-based aqueous electrolyte*". First of all, the electrochemical behavior of the cells on two different carbon materials was tested – microporous activated carbon (YP-50 F) and micro/mesoporous carbon black (BP2000). It was found that carbon black as the electrode material ensures higher capacitance values and better charge propagation than microporous one.

Due to the relatively high price of the gold nanoparticles, different concentrations of this additive (0.1-4 $nmol \cdot L^{-1}$) for the electrolytic solution were tested. The cells operating in KSCN solution and nanoparticles-modified electrolytes were charged and discharged with various current densities (0.5 – 20 $A \cdot g^{-1}$) to compare the capacitance values reached, depending on AuNPs concentration and capacitance retention. The results of these experiments are presented in **Fig. P2.1**. It is seen, that the addition of AuNPs (no matter the concentration) allows the capacitance of the ECs to be increased. Moreover, the capacitance retention is better for nanoparticle-modified systems. Nanoparticles were introduced to the electrolytic solutions in form of a stabilized suspension in phosphate-buffered saline. Therefore, the impact of this additive needed to be determined as well. The same experiment was performed for the cell operating in KSCN with phosphate-buffered saline. Capacitance for this cell was slightly increased due to phosphate-buffered saline addition. Nonetheless, in gold nanoparticles-modified electrolytes, cells' capacitance was significantly higher.

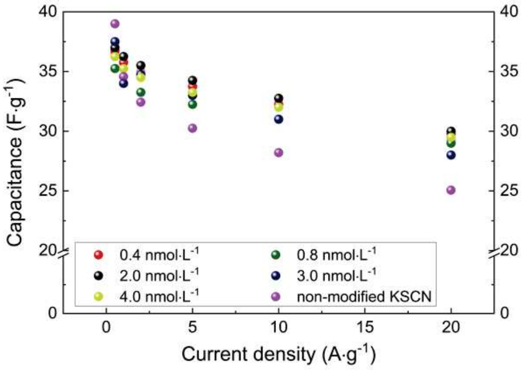


Fig. P2.1. Capacitance (calculated per both electrodes' mass) in the function of applied current density obtained for the systems operating in 7 mol·L^{-1} KSCN-based electrolytes (non-modified and modified with AuNPs)

In spite of the above-mentioned benefits of gold nanoparticles addition to the thiocyanate-based electrolyte for EC application, there are also others that need to be mentioned. It was found that nanoparticles can be considered as the factor for better power retention (detailed comparison of energy/power characteristics of the ECs operating in all the proposed electrolytes is provided at the end of this chapter). Moreover, thanks to AuNPs' presence in the electrolytic solution also the ECs lifetime was prolonged – from 8 500 up to 18 500 cycles. But the question arose – what was the reason for such a significant improvement in tested cells' performance? Firstly, the impact of gold nanoparticles on the redox activity/response of thiocyanate anions was investigated. The cell was charged and discharged with constant current up to 0.8 V and 1.6 V, in a two-electrode configuration with the reference, to determine the operating potentials of each electrode and compare the redox behavior of the positive electrode with the behavior of the electrode polarized in non-modified 7 mol·L^{-1} KSCN solution. It was noticed that there is no difference in redox response for both tested cells, proving that added nanoparticles do not change the redox reaction ongoing during the cell operation. Moreover, *post mortem* analyses of the electrodes were performed with Raman spectroscopy and compared with the spectrum of the pristine carbon electrode (**Fig. P2.2**). For the electrodes investigated directly after the electrochemical tests (red and green curves), except typical peaks coming from carbon material (D- and G-bands, at 1315 and 1595 cm^{-1}, respectively), peaks related to the C≡N (2050 cm^{-1}) and C–S (737 cm^{-1}) bands are observed [206, 214]. Their intensity is higher in the case of the electrode which was operating with AuNPs-modified electrolyte, suggesting higher concentration of the considered species. It is also seen, that after washing the electrodes with water, these peaks are not visible anymore (for both KSCN and nanoparticle-modified solutions; only one result presented in **Fig. P2.2**). Hence, it can be assumed that there are no bonds created between SCN$^-$ anion and carbon material.

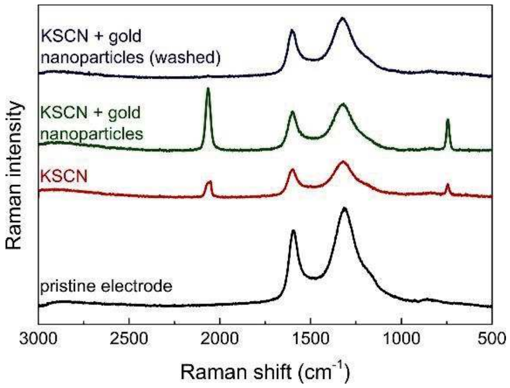


Fig. P2.2. Raman spectra recorded for the pristine electrode and the positively polarized electrodes after operating in non-modified KSCN electrolyte and the electrolyte with AuNPs addition

It was also interesting to evaluate if the addition of the nanoparticles to the electrolytic solution had a positive impact on the cell with pure EDL formation. The additional tests were thus performed and the energy and power of the EC with Li_2SO_4 as electrolyte were determined (**Fig. P2.3**). It is seen that the values obtained for the systems operating in non-modified and AuNPs-modified electrolytes are comparable, showing that this additive has no impact on typical capacitive systems. So now, are the interactions between gold nanoparticles with KSCN-based electrolyte specific, or is it possible to improve the EC performance if another redox-active electrolyte is used? To verify this issue, the same tests were performed for the systems assembled with KI electrolytes (modified and non-modified with AuNPs) and the results are presented in (**Fig. P2.3**).

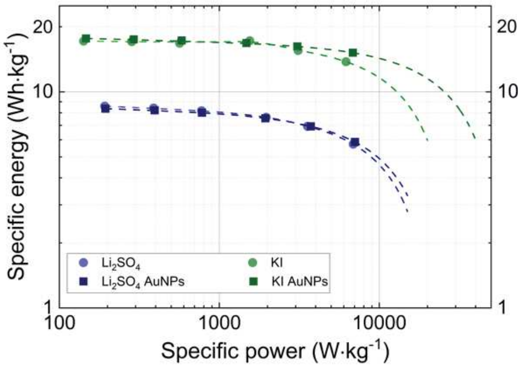


Fig. P2.3. Ragone plot for the cell operating in 1 mol·L^{-1} Li_2SO_4 solution (blue curves) and 2 mol·L^{-1} KI solution (green curves); both electrolytes were tested with and without AuNPs addition

The cell performance was improved by nanoparticles addition – just likewise for thiocyanate-based systems. Therefore, it can be concluded that gold nanoparticles can be used as a performance improvement agent in the cells operating in redox-active electrolytes (at least in halides and pseudohalides solutions).

It is claimed that AuNPs increase the electrode conductivity and create the active sites for thiocyanates' activity, according to the schematic description presented in **Fig. P2.4**. That being the case, the role of nanoparticles is related to the increased reaction rate (electron transfer) and higher efficiency of these processes, even during long-term operation.

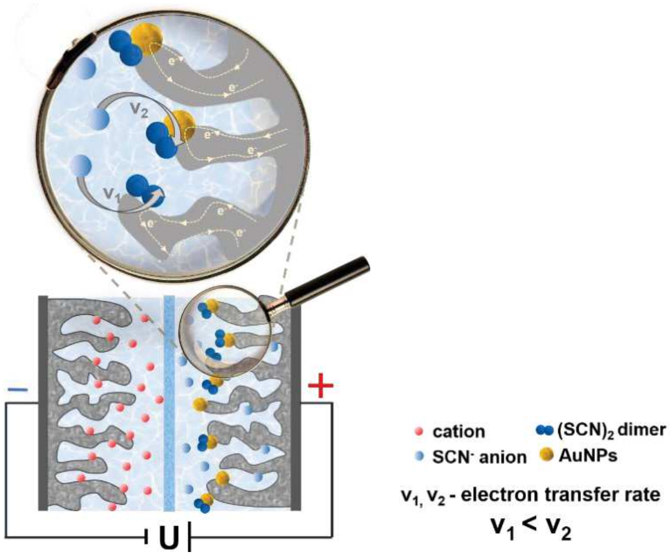


Fig. P2.4. Scheme describing the possible role of gold nanoparticles, as the additive to the electrolytic solution, on the redox activity of thiocyanate anion at the positively polarized electrode

An alternative solution to aqueous thiocyanate-based electrolytes was proposed in the paper **P3** "*Redox activity of selenocyanate anion in electrochemical capacitor application*" – potassium selenocyanate – KSeCN. These electrolytic solutions have also high conductivity (comparable to thiocyanate-based ones). Due to the higher reactivity of the selenium atom in comparison to sulfur one, electroactivity of the redox couple $2SeCN^{-}$ / $(SeCN)_2$ occurs at a lower potential than electroactivity of couple $2SCN^{-}$ / $(SCN)_2$, and it is rather comparable to the iodide activity (**Fig. 14**). In **Fig**. **P3.1a** it is clearly seen that the positive electrode operates in a very narrow potential range and mostly current coming from redox reactions is recorded, whereas the negative electrode is characterized by typical capacitive behavior. Because of these similarities and high enough conductivity, 2 $mol \cdot L^{-1}$ KSeCN solution was chosen for further studies. For EC's construction micro/mesoporous carbon material was used because this one was chosen as the optimal one for thiocyanate-based electrolytes and also the molecules' sizes are similar in both cases. Based on the two-electrode experiments performed with CV technique (**Fig**. **P3.1b**), capacitance increase is seen just after exceeding 0.1 V, whereas for the KSCN-based cell this increase was noticeable at the voltage higher than 1.4 V at stainless steel as current collectors. Maximum operating voltage for KSeCN-based cell (1.4 V) exceeds the theoretical voltage of water decomposition, but it is still lower than it was reached for KSCN-based systems (**P1**).

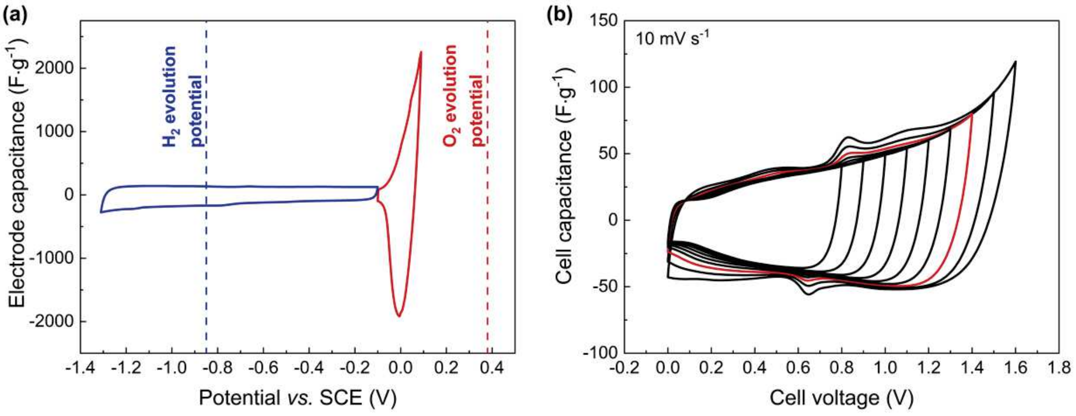


Fig. P3.1. (a) Electrode capacitance in the function of potential applied recorded for both electrodes separately in a three-electrode set-up and **(b)** the cell capacitance with indicated maximum operating voltage of such a system – 1.4 V

EC operating in KSeCN solution as the electrolyte suffers from relatively high self-discharge and leakage current. For all the investigated electrolytes (in the frame of papers **P1-P3**) the same experimental protocol was applied for determining SD and LC parameters. The results are presented in **Tab. 1**. For both KSCN-based cells, the voltage loss during 6 hr of SD measuring is 38%, whereas for the system operating in KSeCN solution the voltage loss is higher than 70% (despite lower maximum voltage). As LC is a very sensitive parameter, strongly dependent on the external conditions and the cell assembling as well, it can be slightly different during several tests. During these experiments measured LC was very high, above 500 mA·g^{-1}, however in some cases it could be lower (because in paper **P3** during galvanostatic charge/discharge experiments current density 0.5 A·g^{-1} was used and it was possible to charge the system up to maximum operating voltage). However, even if the LC was lower than 500 mA·g^{-1}, it is still much greater than the values measured for the EC operating with thiocyanate solutions (~20 mA·g^{-1}).

Tab. 1. Self-discharge (the voltage reached after 6 hr of open circuit conditions) and leakage current (measured during 2 hr of cell hold at maximum voltage U_{max})

Electrolyte	U_{max}	SD	LC
P1. KSCN	1.6 V	0.6 V	21 mA·g^{-1}
P2. KSCN + AuNPs	1.6 V	0.6 V	24 mA·g^{-1}
P3. KSeCN	1.4 V	1 V	> 500 mA·g^{-1}

Definitely, a long cycle-life of the electrochemical capacitor operating in KSeCN solution can be claimed as an advantage. It is expected that such a system can operate at 1.4 V for 30 000 cycles.

As pseudohalides aqueous solutions are promising electrolytes for ECs, with stable electrochemical redox response, an ionic liquid with selenocyanate anion (1-ethyl-3-methylimidazolium selenocyanate [EMIm$^+$][SeCN$^-$]) was synthesized and applied in EC, in order to extent the maximum operating voltage of the cell. The results of this work are described in the paper **P4** entitled *Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors*. Physicochemical parameters of [EMIm$^+$][SeCN$^-$] were comparable to other ILs popular for ECs application (low viscosity 17 mPa·s^{-1} and relatively high conductivity 25 mS·cm^{-1}). The effect of the current collector was examined (stainless steel and aluminum collectors were compared). The electrochemical behavior of both electrodes was investigated in a two-electrode set-up with the reference electrode. The cells were charged up to 2.3 V (with 0.1 V step), and the potential of the electrodes was measured at each step (**Fig. P4.1**).

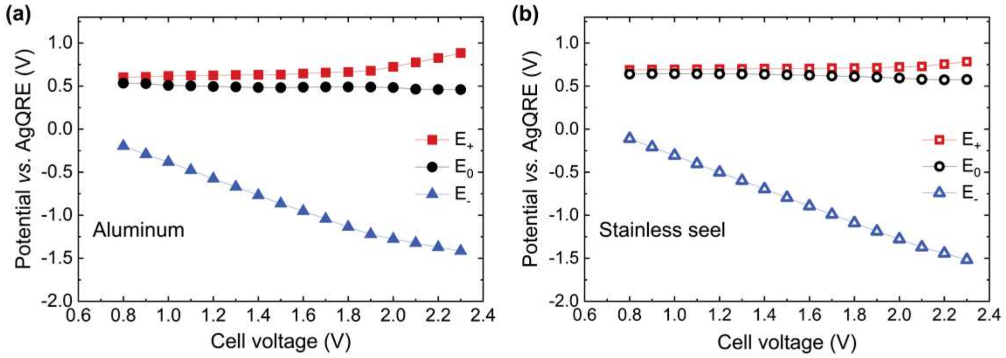


Fig. P4.1. The potentials of the electrodes measured for various voltages (from 0.8 V up do 2.3 V) at **(a)** aluminum and **(b)** stainless steel current collectors

As expected (based on the results from paper **P3**), the positive electrode does not change its potential significantly (as the electrode with major contribution of redox processes coming from selenocyanate anion activity), whereas the negative electrode extents its potential range in order to balance the charge. At aluminum collectors an increase of the positive electrode's potential is observed when the applied voltage is higher than 2 V, suggesting some additional processes, that can be related to the electrolyte decomposition or the electrode oxidation.

Capacitance value reached for [EMIm$^+$][SeCN$^-$]-based cell is high in comparison to other systems with ILs as electrolytes (the table with comparison with the other systems is provided in **P4**). However, the operating voltage of the tested system is relatively low – 1.5 V and, as a consequence, the energy density is considered moderate, but the power rate is reasonable.

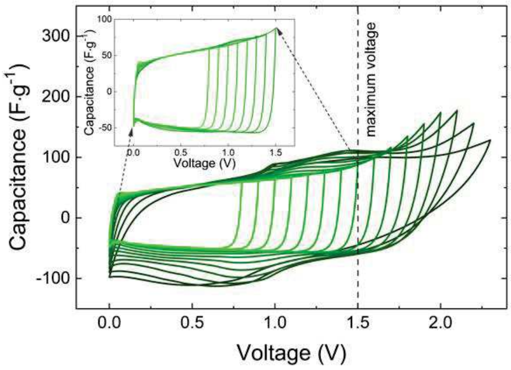


Fig. P4.2. Capacitance (calculated per active mass in the system) in the function of applied voltage

The maximum voltage was chosen based on several tests and the reason of that is clearly seen in **Fig. P4.2**. Up to 1.5 V electrical double-layer charging with well-pronounced redox activity and reversibility is observed. Above this voltage, additional peaks appear, the curve's shapes are deteriorated and the efficiency of ongoing processes is noticeably lower.

Cycling tests were also performed at both studied current collector' types. For the system assembled with stainless steel current collectors, 20% of the capacitance loss is reached after 10 000. In the case of the cell with aluminum current collectors after the same number of cycles, 10% of capacitance loss is seen. It is expected that the lifetime of the EC operating with [$EMIm^+$][$SeCN^-$] as the electrolyte is more than 30 000 cycles at these conditions (1 $A·g^{-1}$).

The papers discussed above present new possible redox-active electrolytes for ECs, where porous activated carbon electrodes are employed. However, the question should be asked: **do such solutions really improve the energy and power of the EC**? To answer this question the Ragone plot is presented, where the energy and power values are calculated based on the galvanostatic charge/discharge profiles for the indicated maximum voltages (**Fig. 16**).

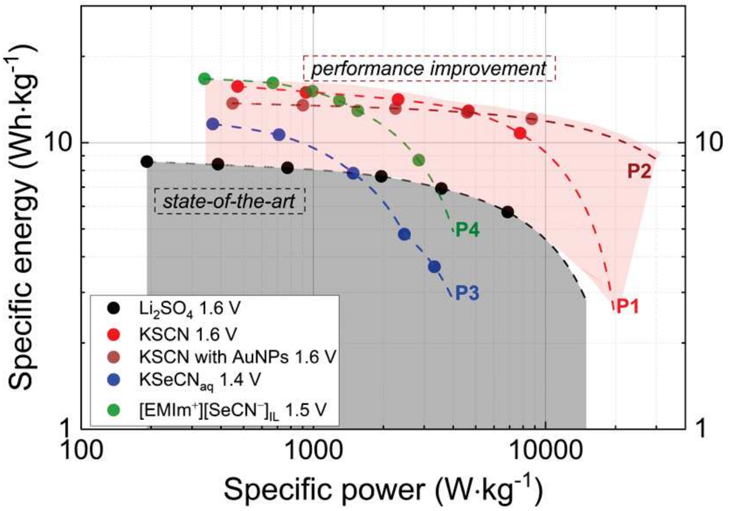


Fig. 16. The Ragone plot comparing the energy and power rate of ECs operating in different redox-active electrolytes – aqueous solutions of 7 mol·L^{-1} KSCN, 7 mol·L^{-1} KSCN modified with gold nanoparticles and 2 mol·L^{-1} KSeCN, ionic liquid – [$EMIm^+$][$SeCN^-$], and 1 mol·L^{-1} neutral solution of Li_2SO_4, as a well-known electrolyte for ECs

The specific energy values of the ECs assembled with redox-active electrolytes, at relatively low current densities, are significantly higher than the ones reached in Li_2SO_4 solution as the electrolyte. However, it is seen that selenocyanate-based electrolytes are characterized by moderate power, which can be considered as the main disadvantage of these systems. The best energy/power characteristic is described in the case of thiocyanate-based EC (whether modified with gold nanoparticles or not) – high energy, even at relatively high current densities applied, and power comparable to Li_2SO_4-based system. Such a comparison proves that is it possible to improve the most important operating parameters of EC by employing pseudohalide solutions as redox-active electrolytes.

CHAPTER III

Studies of the electrochemical capacitor charging mechanism with the electrochemical dilatometry

One publication attached:

P5. Galek P., Bujewska P., Donne S., Fic K., Menzel J., *New insight into ion dynamics in nanoporous carbon materials: An application of the step potential electrochemical spectroscopy (SPECS) technique and electrochemical dilatometry*, Electrochimica Acta 377 (2021) 138115

and unpublished data concerning **Impact of electrolyte pH on the ion population at the electrode/electrolyte interface monitored by electrochemical dilatometry**

Summary of the publication and data obtained

The description of the fundamental studies' importance is included in the Introduction (**Chapter I**). In the case of the electrochemical capacitors development, it is worth to take a look at the ionic fluxes during the device operation. First of all, the work **P5** entitled *New insight into ion dynamics in nanoporous carbon materials: An application of the step potential electrochemical spectroscopy (SPECS) technique and electrochemical dilatometry* focuses on the mechanism of the EC charging when the ionic liquid is used as the electrolyte. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [$EMIm^+$][$TFSI^-$]) was selected due to the similar ion sizes (~0.7 nm) [215]. Additionally, two different carbon materials are tested – activated carbon Kuraray YP-50F and activated carbon black BP2000. SSA are comparable for both materials, but they are characterized by different PSD – YP-50F is typical microporous carbon, whereas BP2000 is a micro/mesoporous material, with an external porosity. The choice of the IL and the electrode materials were well thought. Due to similar anion and cation sizes, it is possible to notice the differences in electrode height changes that denote the variation in charge storage mechanisms at the positively and negatively polarized electrodes. Moreover, the impact of the material porosity on the charge accumulation can be also determined.

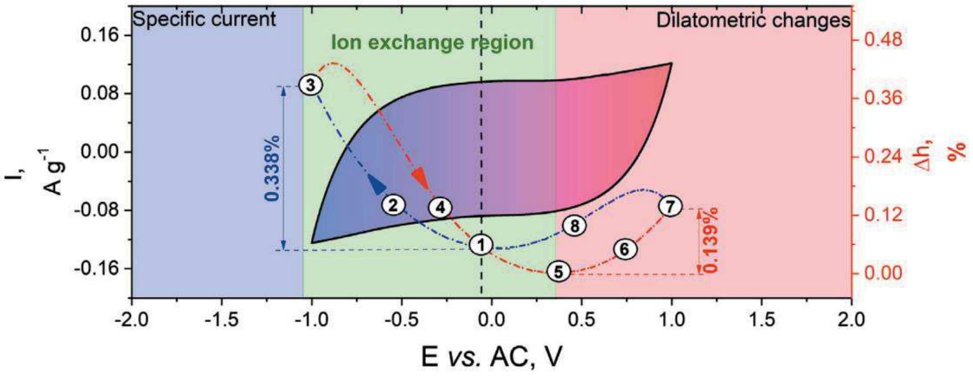


Fig. P5.1. Cyclic voltammogram recorded for the microporous electrode YP-50F, polarized in both directions with the height changes measured simultaneously

It was detected that in the case of the microporous electrode polarized negatively, two successive processes can be distinguished – the ion-exchange mechanism and counter-ion adsorption (**Fig. P5.1**). SPECS studies were also performed, as they can help distinguish and quantify current components and, in consequence, describe the charge storage mechanisms of the polarized electrodes [216, 217]. It was noticed that adsorption of $EMIm^+$ cation required providing a higher charge than the one necessary during the ion-exchange mechanism. When the electrode was polarized positively, initially, the charge was balanced with co-ion desorption and ion exchange mechanisms. Moreover, with increasing voltage and, in consequence, increasing potential of this electrode, counter-ion contribution in EC charging seems to be predominant.

In the case of micro/mesoporous material – BP2000, the changes of the electrode height change are comparable for the negatively and positively polarized electrodes (**Fig. P5.2**). The dilatometry results correlated with the SPECS data led to the assumption that the charge balancing is realized by an ion-exchange mechanism with counter-ions adsorption. However, the delayed response of anions is seen during the positive polarization. In the ion-exchange region shrinkage of the electrode is visible, suggesting that the cations leave the material porosity faster than the anions fill it. Moreover, when the polarization is reversed, there is an electrode swelling, more pronounced than the one observed at reversed polarization at negative potentials. For the potentials exceeding the ion exchange area in both positive and negative direction, the permselective adsorption of anions and cations, respectively, is realized in the same way, which is reflected as the electrode height increase with the same slope.

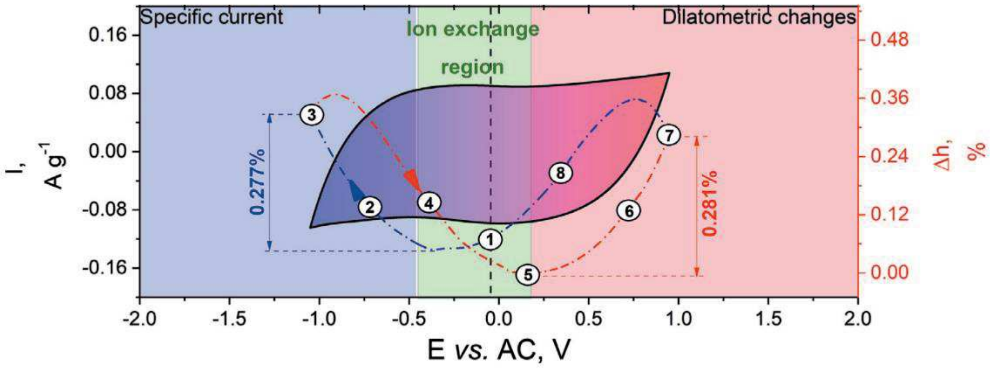


Fig. P5.2. Cyclic voltammogram recorded for the micro/mesoporous electrode BP2000, polarized in both directions with the height changes measured simultaneously

Based on this work (**P5**) it can be concluded that the mechanism of EC charging strongly depends on electrode material texture. Moreover, the same cation and anion size notwithstanding, the electrode height change during positive and negative polarization is not the same, suggesting that aside from the ions' size, other factors impact the ionic fluxes during the cell operation.

Height change of the electrodes in EC operating in an aqueous electrolyte (1 mol·L^{-1} Li_2SO_4 solution) was also measured. The electrodes were prepared from microporous AC Kuraray YP-50F. **The aim of this work was to determine the influence of the solution's pH on the charge storage mechanism with electrochemical**

dilatometry. Therefore, Li_2SO_4 solutions of various pH – 6, 9 and 12 were prepared. Electrochemical tests were performed to verify how exactly pH value influences the electrochemical behavior of the system. The cells with these electrolytes were assembled, in two-electrode with the reference configuration, and charged up to 1.6 V. The operating potentials of both electrodes were determined and then each electrode was polarized separately with cyclic voltammetry (5 $mV \cdot s^{-1}$). The results of these experiments are presented in **17**.

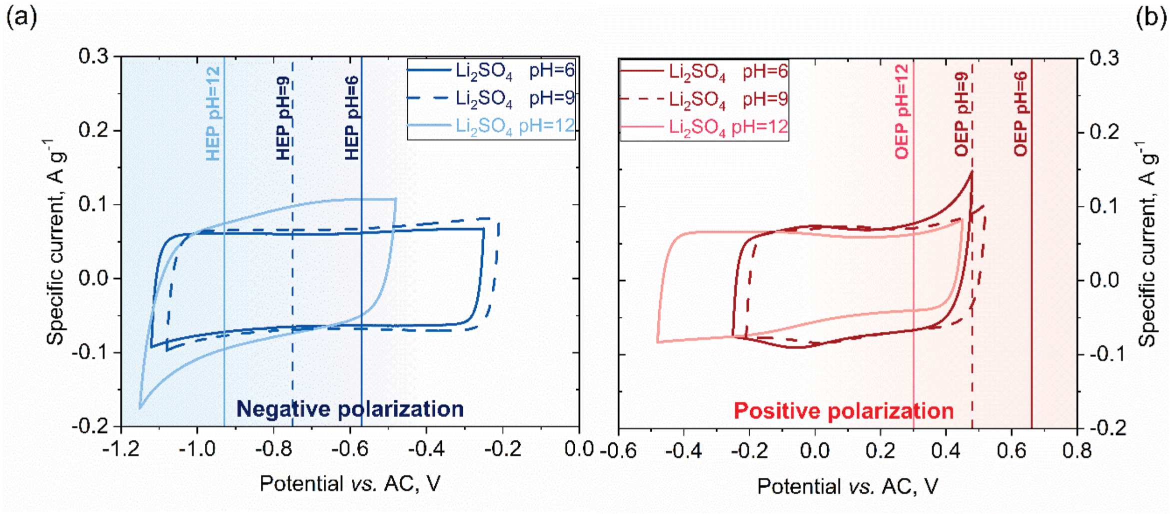


Fig. 17. Cyclic voltammograms recorded for the electrodes polarized negatively **(a)** and positively **(b)** in sulfate-based electrolytes of different pH

The maximum and minimum potentials are similar for each electrolyte. Despite this fact, the electrochemical behavior is different in each case which is related to the hydrogen and oxygen evolution potentials (HEP and OEP, respectively). It explains a higher current response for the positively polarized electrode in the electrolyte of pH 12. Theoretically, such an increase was also expected for the alkaline electrolyte. However, the pH value measured near the electrode surface after the experiment was about 9, suggesting that during the experiment local pH changes occur and OEP can be shifted towards higher values. Based on the presented voltammograms can be concluded that the electrodes in the electrolytes of pH 6 and 9 exhibit comparable characteristics, as opposed to the electrolyte of pH 12. Hence, different mechanisms of charge storage are assumed depending on the lithium sulfate solution pH.

Changes in the height of the electrode were measured simultaneously. The results are presented in **Fig. 18**. One should take into account that the electrode dilatation equals zero is set to 0 V *vs.* AC. Hence, it should be considered as a relative value. The most important is the percentage change, not the value itself. If compare the behavior of the negatively polarized electrodes, in both cases constant electrode expansion is seen. However, the cations' movement to the electrode porosity seems to have different characteristics. In the electrolyte of pH 9, the lower the potential the faster the electrode expansion. For the electrode operating in the electrolyte of pH 12 at the whole potential range the slope of the curve is constant. Moreover, when the polarization is reversed, lithium cations still enter the material porosity (electrode height increase; marked as a response shift). In the more alkaline electrolyte, this shift is definitely less pronounced. It shows that the expelling of the cations from the electrode pores is hindered in lower pH.

Based on the curves recorded during the positive polarization of the electrodes is it seen that the solution pH strongly impacts the anions' movement and the dilatometric response of the electrode. In the case of the Li_2SO_4 solution of pH 9, when potential 0V *vs.* AC is exceeded, the electrode shrinkage is still observed. Based on the literature it is expected that first the cations are removed from the electrode material to balance the electrode charge [16]. Then the ions exchange occurs – at the same time cations are still expelled and the anions are attracted to the electrode surface, and they can penetrate its pores. For the potential higher than +0.15 V *vs*. AC the electrode expansion is observed. It can lead to the conclusion that for such potentials, anions insertion has a larger contribution to the electrode charge balancing than the cations expulsion. For the electrode polarized in the alkaline electrolyte, only the electrode shrinkage is observed. Hence, it seems, that the charge balancing in higher pH is realized by removing cation from the electrode material. It would be to some extent in contrast to the previously presented mechanism for ECs. To verify this issue, an additional test with 1 mol·L^{-1} LiOH solution was performed. The hydroxide solution was chosen, because it is composed of Li^+, H_3O^+ and OH^- ions, and in Li_2SO_4 solution number of OH^- anions is also considerable.

The maximum operating voltage of the cell operating in LiOH solution is lower than for sulfate salts-based electrolytes (1.4 V *vs*. 1.6 V) what is seen at the potential range in **Fig. 18**. The dilatometry data shows that the electrodes behavior is similar for the two tested alkaline electrolytes. As for the negative polarization such results are as expected – in both cases Li^+ are responsible for EDL formation, it is not co clear for the positive polarization. It was believed that SO_4^{2-} anions are attracted to the electrode surface and balance the charge of the electrode. However, if there is no SO_4^{2-} anions in LiOH solution and the behavior of the electrodes looks alike, it can be assumed that hydroxide anions are involved in this process. Their concentration in alkaline Li_2SO_4 solution is three orders of magnitude larger than in pH=9. Additionally, their mobility [14] is higher than sulfate anion ($21\cdot10^{-8}$ *vs.* $8\cdot10^{-8}\cdot m^2\cdot s^{-1}\cdot V^{-1}$, respectively). Hence, OH^- can be easier attracted to the electrode surface whereas $SO4^{2-}$ anions transport requires a remarkably high driving force.

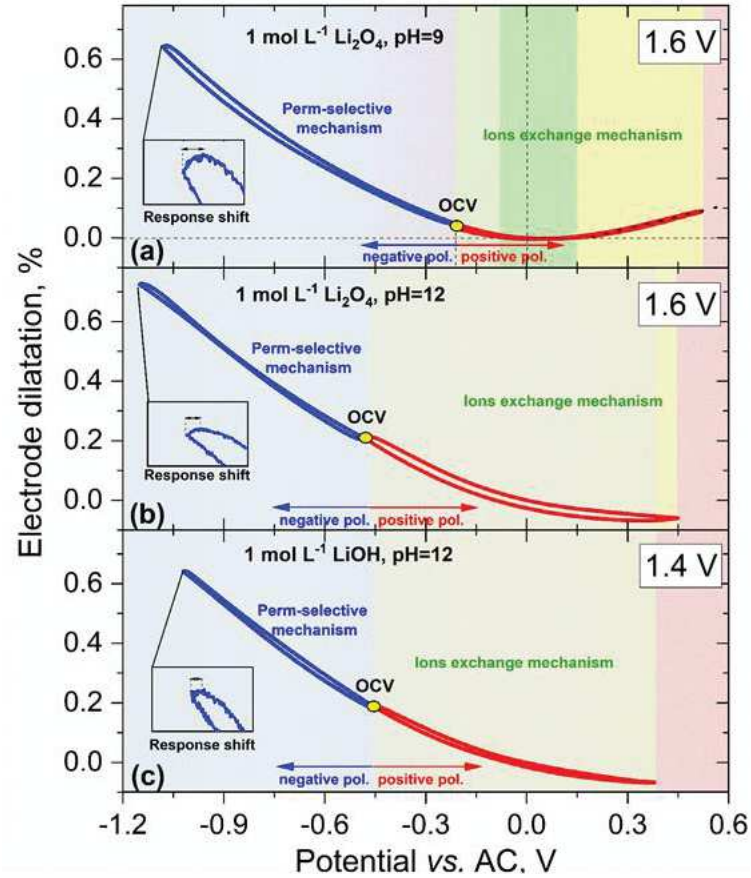


Fig. 18. The electrode dilatation for the electrodes polarized negatively (blue curves) and positively (red curves) in 1 mol·L^{-1} Li2SO4 of pH **(a)** 9, **(b)** 12 and **(c)** 1 mol·L^{-1} LiOH

It can be concluded that the electrochemical behavior of the electrodes and, in consequence, the device strongly depends on the electrolyte pH. With increasing pH, the OH^- contribution on charge storage is more pronounced. Performed studies prove, that the mechanism of charge and discharge of the EC should be examine specifically for the electrode material and electrolyte solution. Probably, it is not possible to present one general charge storage mechanism of EDL formation even for the solutions of the same salt. There are many factors that should be taken into account.

These studies were performed as preliminary studies for the description of charge storage mechanism in pseudohalides-based electrolytes.

SUMMARY

General summary

As the electrochemical capacitors are characterized by rather moderate energy, it is challenging to improve this parameter while maintaining high power. Therefore, redox-active electrolytes are very often used as a source of additional charge that can be stored at the electrode/electrolyte interface and, in consequence, increase the energy of the device.

The studies performed as part of this doctoral dissertation concern the application of new highly conductive redox-active solutions as electrolytes for electrochemical capacitors. Different aqueous solutions were proposed:

- thiocyanate-based electrolytes with alkali metals and NH^+ cation,
- 7 $mol \cdot L^{-1}$ KSCN modified with gold nanoparticles in various concentrations and
- 2 $mol \cdot L^{-1}$ KSeCN.

The experiments with various cell components were performed – different carbon materials were used, the influence of current collectors on the operating parameters of ECs was investigated, the solutions of different concentrations were used as electrolytes. All of the most important parameters of aqueous-based electrochemical capacitors studied in the frame of the doctoral thesis are collated in **Fig. 18** as a radar chart. The specific energy was significantly improved by introducing redox-active electrolytes. Additionally, gold nanoparticles allow higher power of the device to be reached and enhanced the cyclability of the system. However, it is clearly seen that EDLC exhibit definitely better cycle-life.

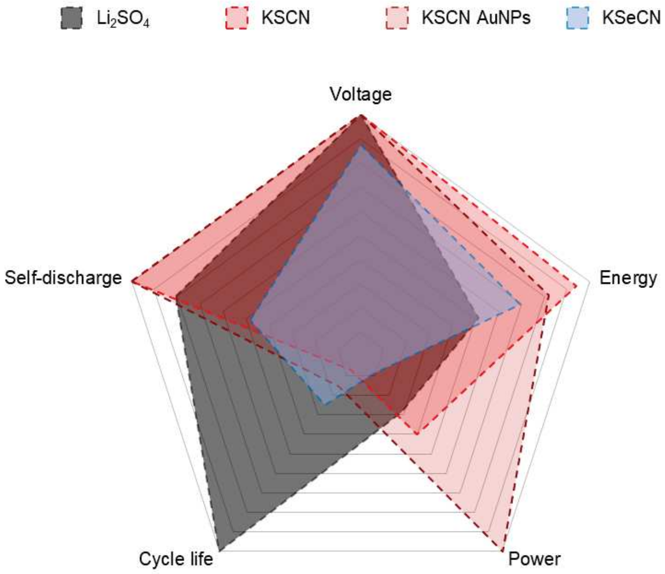


Fig. 19. The radar chart comparing the most important operating parameters of the investigated electrochemical capacitors

Besides aqueous electrolytes, ionic liquid with selenocyanate anion [EMIm$^+$][SeCN$^-$] was also considered as the electrolyte for EC. The effect of current collectors' type was also checked.

Through the experiments conducted, data analysis and comparing the results with the state-of-the-art it is clearly seen, that **all the proposed pseudohalide solutions can be successfully applied in the tested technology**. It allows **the research hypothesis to be confirmed**. As expected, due to redox reactions ongoing during charge and discharge the capacitance of the cells was higher and the energy values were improved. Significantly better cells performance is noticed in comparison to the ECs with well-known lithium sulfate solution as the electrolyte. However, it was not possible to design the cell with enhanced energy and power values in comparison to iodide-based systems.

The charge storage mechanism of the EC operating in non-aqueous electrolyte and aqueous solution (1 mol·L^{-1} Li_2SO_4) was described. In the case of [EMIm$^+$][TFSI$^-$] as the electrolyte, the electrode materials of different porosity (micro- and micro/mesoporous) were used and the mechanisms were compared. For the aqueous-based system, the influence of the solution's pH on the ionic fluxes in the microporous electrode vicinity was investigated. It can be concluded that the processes ongoing the systems need to be studied and elucidated individually, because there is no general and universal description of charge storage mechanism in ECs.

Main achievements:

- ECs can effectively operate with inorganic pseudohalide solutions as electrolytes, reaching:
    - maximum voltage 1.4 V with an expected lifetime of 30 000 cycles – in 2 mol·L^{-1} KSeCN solution, specific energy of such system is 12 Wh·kg^{-1},
    - maximum voltage 1.4 V with a lifetime of at least 100 000 cycles – in 5 mol·L^{-1} NH_4SCN solution,
    - maximum voltage 1.6 V with a lifetime of 10 000 cycles – in 7 mol·L^{-1} KSCN solution; specific energy of such system is 16 Wh·kg^{-1},

when micro/mesoporous electrode material (BP2000) is used.

- Gold nanoparticles were found advantageous additive to the electrolytic solution, that allow power characteristics of the EC to be improved.
- Self-discharge of the cells operating in KSCN solution as electrolyte is moderate, whereas in KSeCN solution the voltage drop in time is significantly higher.

- Ionic liquid – $[EMIm^+][SeCN^-]$ can be used as the electrolyte for EC; it allows 1.4 V to be reached when microporous electrodes are employed; the lifetime of IL-based system is 10 000 cycles on stainless steel current collectors and about 30 000 cycles on aluminum collectors.
- Electrochemical dilatometry can be useful for studies the charge storage mechanism at the polarized electrode.
- The mechanism of charge storage accumulation within the electrode polarized positively and negatively is different. Nonetheless, it cannot be directly related to the cation and anion sizes because despite the comparable ion sizes in investigated IL, i.e. $[EMIm^+][TFSI^-]$, the electrode dilatation was not symmetric when the microporous electrode was considered.
- The charge storage mechanism in aqueous-based electrolytes depends on the solution pH.
    - In strongly alkaline Li_2SO_4 solution this mechanism is similar to the one determined for LiOH as electrolyte.
    - Hydroxide anion, as a more mobile one than SO_4^{2-}, is assumed to be responsible for EDL formation at the positive electrode.
    - Charge accumulation at the negatively polarized electrode also vary at different electrolyte pH, what can be connected to different Li^+ / H^+ ratio as well as variable solvation sell of Li^+, influenced by solution pH.

There are also issues that require further studies in order to improve the performance of the cell and limit their drawbacks. First of all, self-discharge should be limited. From the practical point of view, it is one of the most important properties of these devices. Secondly, 1.4 V reached in IL as the electrolyte seems to be a relatively low value (taking into account that the cells operating in non-aqueous electrolytes are able to work at a voltage higher than 2 V). It was proven that the ILs with pseudohalide anions are not easy for drying and since the water content in IL was not determined, there is a possibility that it was too high, causing side reactions (electrolyte decomposition).

To understanding the mechanism of charge storage in ECs operating in redox-active electrolytes series of experiments need to be performed. It seems, that electrolyte dilatometry coupled with SPECS would be useful for this purpose. However, as the redox reactions can also occur at the surface of the polarized electrode, it would be advantageous to employ the technique for determination the ions adsorption at the electrode surface – for example electrochemical quartz crystal microbalance.

SYMBOLS AND ABBREVIATIONS

Abbreviation/Symbol	**Explanation**	**Unit**
A	electrode surface area	m^2
AC	alternating current	
AC	activated carbon	
ACN	acetonitrile	
BET model	Brunauer-Emmett-Teller model	
C	capacitance of EC	F
$C_{/m}$	gravimetric capacitance of the cell	$F\cdot g^{-1}$
C_D	diffusion layer's capacitance	F
C_E, $C_{(+)}$, $C_{(-)}$	capacitance of the electrode, positive and negative one	F
$C_{E/m}$	gravimetric capacitance of the electrode	$F\cdot g^{-1}$
C_s	Stern layer's capacitance	F
CDC	carbide-derived carbon	
CNT	carbon nanotube	
d	distance between the electrodes	m
DC	direct current	
DCA	dicyanoamide anion	
DFT	density functional theory	
E	energy	Wh
EC	electrochemical capacitor	
ECD	electrochemical dilatometry	
EDL	electrical double-layer	

EMIm	1-ethyl-3-methylimidazolium tetrafluoroborate cation	
EQCM	quartz crystal microbalance	
ESR	equivalent series resistance	Ohm
ε_0	vacuum permittivity	$F \cdot m^{-1}$
ε_r	relative dielectric permittivity (dielectric constant)	[-]
FSI	bis(fluorosulfonyl)imide anion	
IL	ionic liquid	
IR	infrared	
LC	leakage current	$A \cdot g^{-1}$
Li-ion	lithium-ion battery	
Li-primary	lithium primary battery	
m_{act}	active mass of the device	g
MV	methyl viologen	
NHE	normal hydrogen electrode	
Ni-MH	nickel-metal hydride battery	
NMR	nuclear magnetic resonance	
P	power	W
PC	propylene carbonate	
PSD	pore size distribution	
q	charge	C
Q	total charge stored in capacitor	C
R_s, $R_{(+)}$, $R_{(-)}$	resistance coming from the separator, positive and negative electrode	Ohm

R'X	haloalkane	
SCE	saturated calomel electrode	
SD	self-discharge	V
SECM	scanning electrochemical microscopy	
SI Unit	The international System of Units	
SSA	specific surface area	$m^2 \cdot g^{-1}$
t	time	hr
TEA	tetraethylammonium cation	
TFSI	bis(trifluoromethanesulfonyl)imide anion	
U	voltage	V
W	work	J
ΔV	potential change	V
Φ	electric potential changes	V
Φ_b	potential at the electrolyte bulk	V
Φ_E	electrode potential	V

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SCIENTIFIC ACHIEVEMENTS

1. Publications

1. **Bujewska P.**, Górska B., Fic K., "Gold nanoparticles for power retention in electrochemical capacitors with KSCN-based aqueous electrolyte", Journal of Power Sources Advances 14 (2022) p. 100087
2. Galek P., **Bujewska P.**, Donne S., Fic K., Menzel J., "New insight into ion dynamics in nanoporous carbon materials: An application of the step potential electrochemical spectroscopy (SPECS) technique and electrochemical dilatometry", Electrochimica Acta 377 (2021) pp. 138115, IF = 6,901
3. Galek P., Maćkowiak A., **Bujewska P.**, Fic K., "Three-dimensional architectures in electrochemical capacitor applications - insights, opinions and perspectives", Frontiers in Energy Research 8 (2020) pp. 1-21, IF = 4,008
4. Fic K., Płatek A., Piwek J., Menzel J., Ślesiński A., **Bujewska P.**, Galek P., Frąckowiak E., "Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte", Energy Storage Materials 22 (2019) pp. 1-14, IF = 16.280
5. Fic K., Górska B., **Bujewska P.**, Béguin F., Frąckowiak E., "Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors", Electrochimica Acta 314 (2019) pp. 1-8, IF = 6.215
6. **Bujewska P.**, Górska B., Fic K., "Redox activity of selenocyanate anion in electrochemical capacitor application", Synthetic Metals 253 (2019) pp. 62-67, IF = 3.286
7. Górska B., **Bujewska P.**, Fic K., "Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors", Physical Chemistry Chemical Physics 19 (2017) pp. 7923-7935, IF= 3.906

2. Publications in conference materials

1. **Bujewska P.**, Górska B., Fic K. "*Nanogold as additive to pseudohalide electrolytes for carbon/carbon electrochemical capacitor*" Carbon 2018, The World Conference on Carbon, Madrid, Spain, 1 - 6 July 2018

3. Granted patents

1. Fic K., Górska B., **Bujewska P.,** Frąckowiak E. "Hybrydowy układ elektrochemiczny" (*Hybrid electrochemical system)* – patent number: **Pat.238543**, application date: 28.03.2018; (WUP 06.09.2021)
2. Fic K., Górska B., **Bujewska P.,** Frąckowiak E. "Kondensator elektrochemiczny" (*Electrochemical capacitor)* – patent number: **Pat.238542**, application date: 13.02.2018; (WUP 06.09.2021)
3. Fic K., **Bujewska P.,** Górska B., Frąckowiak E. "Kondensator elektrochemiczny" (*Electrochemical capacitor)* – patent number: **Pat.237460**, application date: 20.09.2016 (WUP 19.04.2021)
4. Fic K., **Bujewska P.,** Górska B., Frąckowiak E. "Kondensator elektrochemiczny" (*Electrochemical capacitor)* – patent number: **Pat.237459**, application date: 05.09.2016 (WUP 19.04.2021)
5. Fic K., **Bujewska P.,** Górska B., Frąckowiak E. "Kondensator elektrochemiczny" (*Electrochemical capacitor)* – patent number: **Pat.237458**, application date: 05.09.2016 (WUP 19.04.2021)
6. Fic K., **Bujewska P.,** Górska B., Frąckowiak E. "Kondensator elektrochemiczny" (*Electrochemical capacitor)* – patent number: **Pat. 237457**, application date: 05.09.2016 (WUP 19.04.2021)
7. Fic K., Górska B., **Bujewska P.,** Frąckowiak E. "Kondensator elektrochemiczny pracujący w elektrolicie z cieczą jonową" (*Electrochemical capacitor operating in electrolyte containing ionic liquid)* – patent number: **Pat.237466**, application date: 21.11.2016 (WUP 19.04.2021)
8. Fic K., **Bujewska P.,** Górska B., Frąckowiak E. "Kondensator elektrochemiczny" (*Electrochemical capacitor)* – patent number: **Pat.231243**, application date: 28.09.2015 (WUP 28.02.2019)

4. Oral presentations at international conferences

1. **Bujewska P.**, Fic K.,
   "Electrical Double-Layer Formation at Nanoporous Carbon Electrodes with Aqueous Electrolytes of various pH Monitored by Electrochemical Dilatometry"
   72nd Annual Meeting of the International Society of Electrochemistry, Jeju Island, Korea, 29 August – 3 September 2021
2. Fic K., Galek P., Menzel J., **Bujewska P.**, Donne S. W.
   "Demystifying the Electrode/Electrolyte Interface in Carbon-Based Electrochemical Capacitors with Specs Technique and Electrochemical Dilatometry"
   Pacific Rim Meeting on Electrochemical and Solid-State Science PRiME 2020, USA, Honolulu (on-line event), 4 – 9 October 2020
3. Płatek A., Menzel J., **Bujewska P.**, Frąckowiak E., Fic K.
   "Gravimetric and Volumetric Changes of Carbon Electrodes in Electrochemical Capacitors with Aqueous Electrolytes"
   236th ECS Meeting, The Electrochemical Society, Advancing solid state & electrochemical science & technology, Atlanta, Georgia, USA, 13 – 17 October 2019
4. Fic K., Płatek A., Menzel J., Ślesiński A., **Bujewska P.**, Piwek J., Galek P., Frąckowiak E.
   "Operando exploration of the ionic fluxes at the electrode/electrolyte interface for better electrochemical capacitors"
   6th International Conference on Advanced Capacitors (ICAC 2019) Shinshu University, Ueda Campus, Japan, 8 – 12 September 2019
5. Fic K., **Bujewska P.**, Górska B.
   "Redox Active Electrolytes Modified by Nanoparticles – Towards High-Energy Supercapacitors"
   The 2018 MRS Fall Meeting & Exhibit, Boston, Massachusetts, USA, 25 – 30 November 2018
6. Fic K., Menzel J., **Bujewska P.**
   "Natural Antioxidants for Activated Carbon-Based Electrochemical Capacitors with Enhanced Energy and Cycle Life"
   Americas International Meeting on Electrochemistry and Solid State Science AIMES 2018, Cancun, Mexico, 30 September – 4 October 2018
7. Fic K., **Bujewska P.**, Górska B., Frąckowiak E.
   "Au Nanoparticles as Additive to Pseudohalide-Based Electrolytes for High-Energy Electrochemical Capacitors"
   The 2018 MRS Spring Meeting & Exhibit, Phoenix, Arizona, USA, 2 – 6 April 2018

8. Górska B., Fic K., **Bujewska P.**, Frąckowiak E., Béguin F.
   "Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors"
   5th International Symposium on Enhanced Electrochemical Capacitors, Jena, Germany, 10 – 14 July 2017
9. Fic K., Górska B., **Bujewska P.**, Béguin F., Frąckowiak E.
   "Redox Activity of Pseudohalides for Energy Enhancement and Overcharging Protection in Electrochemical Capacitors"
   The 2016 MRS Fall Meeting & Exhibit, Boston, USA, 27 November – 2 December 2016
10. Fic K., Górska B., **Bujewska P.**, Béguin F., Frąckowiak E.
    "Pseudohalide-based Electrolytes for High-Energy Electrochemical Capacitors"
    Pacific Rim Meeting on Electrochemical and Solid-State Science PRiME 2016, USA, Honolulu, 2 – 7 October 2016
11. Fic K., Górska B., **Bujewska P.**, Béguin F., Frąckowiak E.
    "Pseudohalide-based electrolytes for high-energy capacitors"
    67th Annual Meeting of the International Society of Electrochemistry, The Hague, Netherlands, 21 – 26 August 2016
12. Fic K., Górska B., **Bujewska P.**, Béguin F., Frąckowiak E.
    "Pseudohalides as redox active electrolytes for supercapacitors"
    5th International Conference on Advanced Capacitors, Otsu, Shiga, Japan, 23 – 27 May 2016

5. Oral presentations at Polish conferences

1. **Bujewska P.**, Ślesiński A., Fic K., Frąckowiak E.
   "Addition of natural antioxidants for carbon/carbon electrochemical capacitors"
   XII Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe, Nauka – Przemysł' 2019", Ustroń – Jaszowiec, 2 – 5 April 2019
2. Górska B., **Bujewska P.**, Fic K., Béguin F., Frąckowiak E.
   "Carbon-based electrochemical capacitors with pseudohalides redox active electrolytes"
   X Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe", Ustroń – Jaszowiec, 4 – 7 April 2017

6. Poster presentations at international conferences

1. **Bujewska P.**, Górska B., Fic K.
   "Gold nanoparticles as an additive to the electrolyte for electrochemical capacitors – does the size matter?"
   International Symposium on Enhanced Electrochemical Capacitors ISEECap 2019, Nantes, France, 6 – 10 May 2019

2. **Bujewska P.**, Ślesiński A., Fic K., Frąckowiak E.
   "Protecting the positive electrode of electrochemical capacitor against oxidation"
   69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, 2 – 7 September 2018

3. **Bujewska P.**, Górska B., Fic K.
   "Nanogold as additive to pseudohalide electrolytes for carbon/carbon electrochemical capacitor"
   Carbon 2018, The World Conference on Carbon, Madrid, Spain, 1 - 6 July 2018

4. Górska B., **Bujewska P.**, Fic K., Frąckowiak E.
   "Pseudohalides as water-based, redox active electrolytes for electrochemical capacitors"
   The First International Conference on Energy Storage Materials, Shenzhen, China, 18 – 21 November 2017

5. **Bujewska P.**, Górska B., Fic K.
   "Pseudohalides as redox active electrolytes for high-energy carbon/carbon capacitors"
   Carbon for Energy Storage and Environment Protection (CESEP'17), Lyon, France, 23 – 26 October 2017

6. Górska B., **Bujewska P.**, Fic K.
   "The role of pseudohalides in carbon/carbon electrochemical capacitors"
   Carbon 2017, The World Conference on Carbon, Melbourne, Australia, 23 – 28 July 2017

7. **Bujewska P.**, Górska B., Fic K.
   "Pseudohalides as redox active electrolytes for carbon/carbon electrochemical capacitors"
   5th International Symposium on Enhanced Electrochemical Capacitors, Jena, Germany, 10 – 14 July 2017 – **3rd Place Poster Prize Awarded**

8. Jeżowski P., **Bujewska P.**, Fic K., Béguin F.
   "Expansion of activated carbon electrode during EDL charging in various salt aqueous electrolytes"
   67th Annual Meeting of the International Society of Electrochemistry, The Hague, Netherlands, 21 – 26 August 2016

7. Poster presentations at Polish conferences

1. Płatek A., **Bujewska P.**, Menzel J., Frąckowiak E., Fic K.
"Hi-Tech Operando Techniques for Energy Storage Devices"
4th Polish Scientific Networks "Science & Technology", Poznań, 19 – 21 September 2019

2. **Bujewska P.**, Górska B., Fic K.
"Nanoparticle-modified electrolytes for carbon/carbon electrochemical capacitors"
XI Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe", Ustroń – Jaszowiec, Polska, 17 – 20 April 2018

8. Participation in scientific projects

1. Assistant in the frame of European Research Council Starting Grant IMMOCAP "*If immortality unveil…'– development of the novel types of energy storage systems with excellent long-term performance*" under European Unions' Horizon 2020 research and innovation programme; **11.2017 – now**
2. Scientific assistant in the frame of Polish-Swiss research project PSPB 107/2010 INGEC; **01.02.2016 – 30.09.2016**
3. 2015 - Participation in scientific project "High power and high energy electrochemical capacitor" LIDER/18/513/L-4/12/NCBR/2013
4. 2015 - Participation in scientific project "Water based redox active electrolytes for eco-friendly supercapacitors" IUVENTUS PLUS IP2012 010972

9. Short scientific internship

1. A two-week internship **at Institut de Science des Matériaux de Mulhouse (IS2M) in France** under the supervision of Dr. Camélia Matei Ghimbeu in the frame of Polish - French POLONIUM project (2017/18/35182/2016); **30.10.2017 - 10.11.2017**

10. Organizational activities

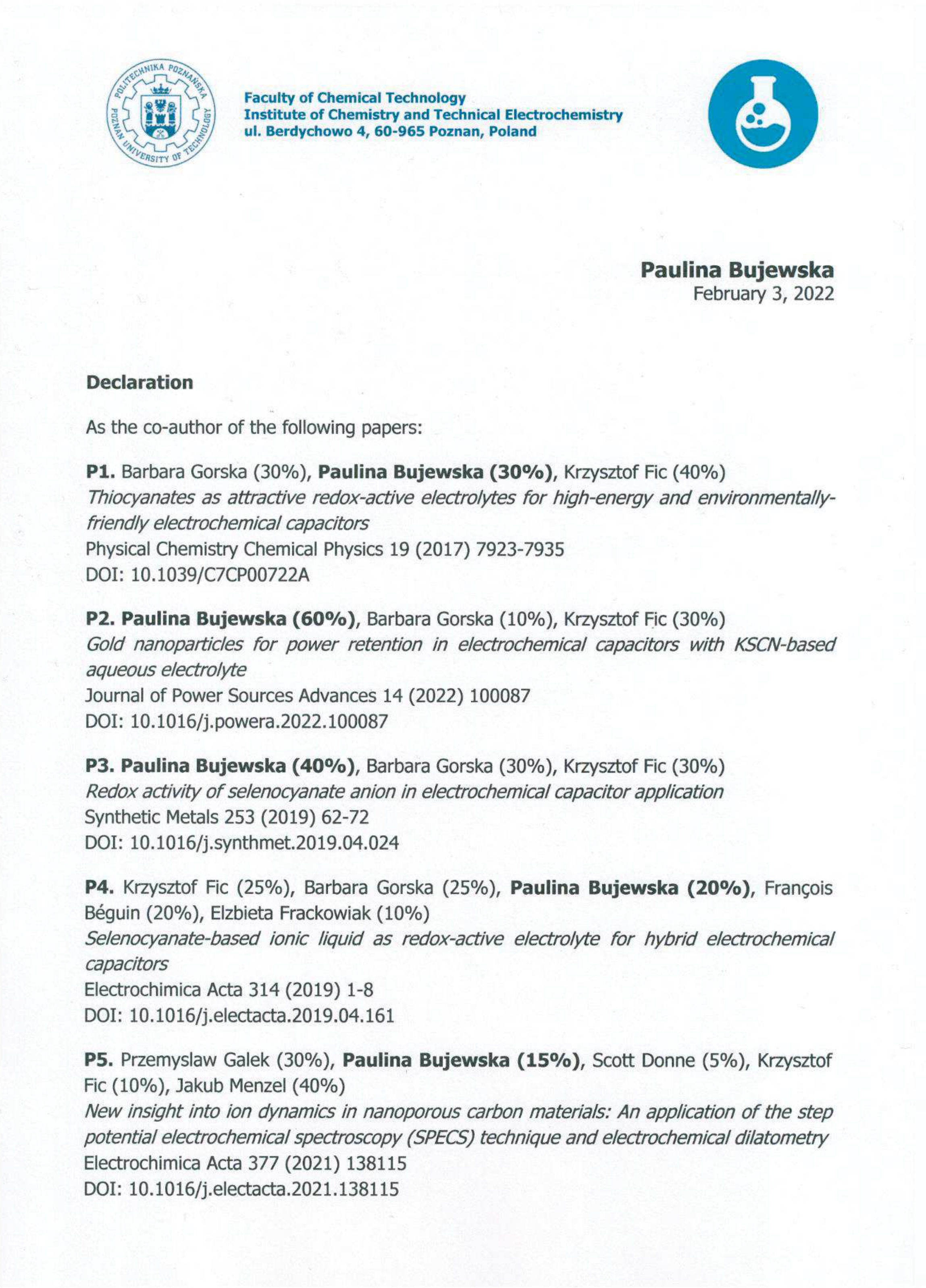
A member of an organizing committee during following workshop/conferences:

1. **The 2nd Scientific Workshop of Polish Carbon Society "New trends in Carbon Science"** targeted at young scientists and PhD students organized at Poznań University of Technology, 27 September 2019
2. **4th Polish Scientific Networks "Science & Technology"**, devoted to modern technology and innovations in various aspects, ranging from social to natural sciences, organized in cooperation with Polish Academy of Sciences at Poznań University of Technology, 19 – 21 September 2019
3. Three editions of summer school **Kuźnia Młodych Talentów** - organized by Academy of Young Scientist from Polish Academy of Sciences at The House of Congresses and Conferences in Jabłonna near Warsaw; the aim of the workshops was to develop the skills necessary for the scientific work and to meet the problems that often are faced by PhD students as young scientists at the beginning of their professional career. Each edition had a different main topic:

- 2 – 5 July 2019: Interdisciplinarity
- 18 – 21 September 2018: Popularization of science
- 27 – 30 September 2017: commercialization of academic-based research

4. **"Komercjalizacja badań – wyzwania dla młodych naukowców"** (*Commercialization of research - challenges for young scientists*) organized by Academy of Young Scientist from Polish Academy of Sciences; the aim of the workshop was to broaden knowledge on the intellectual property rights management; Warsaw 15 – 16 November 2018

CO-AUTHORSHIP STATEMENTS



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Paulina Bujewska
February 3, 2022

Declaration

As the co-author of the following papers:

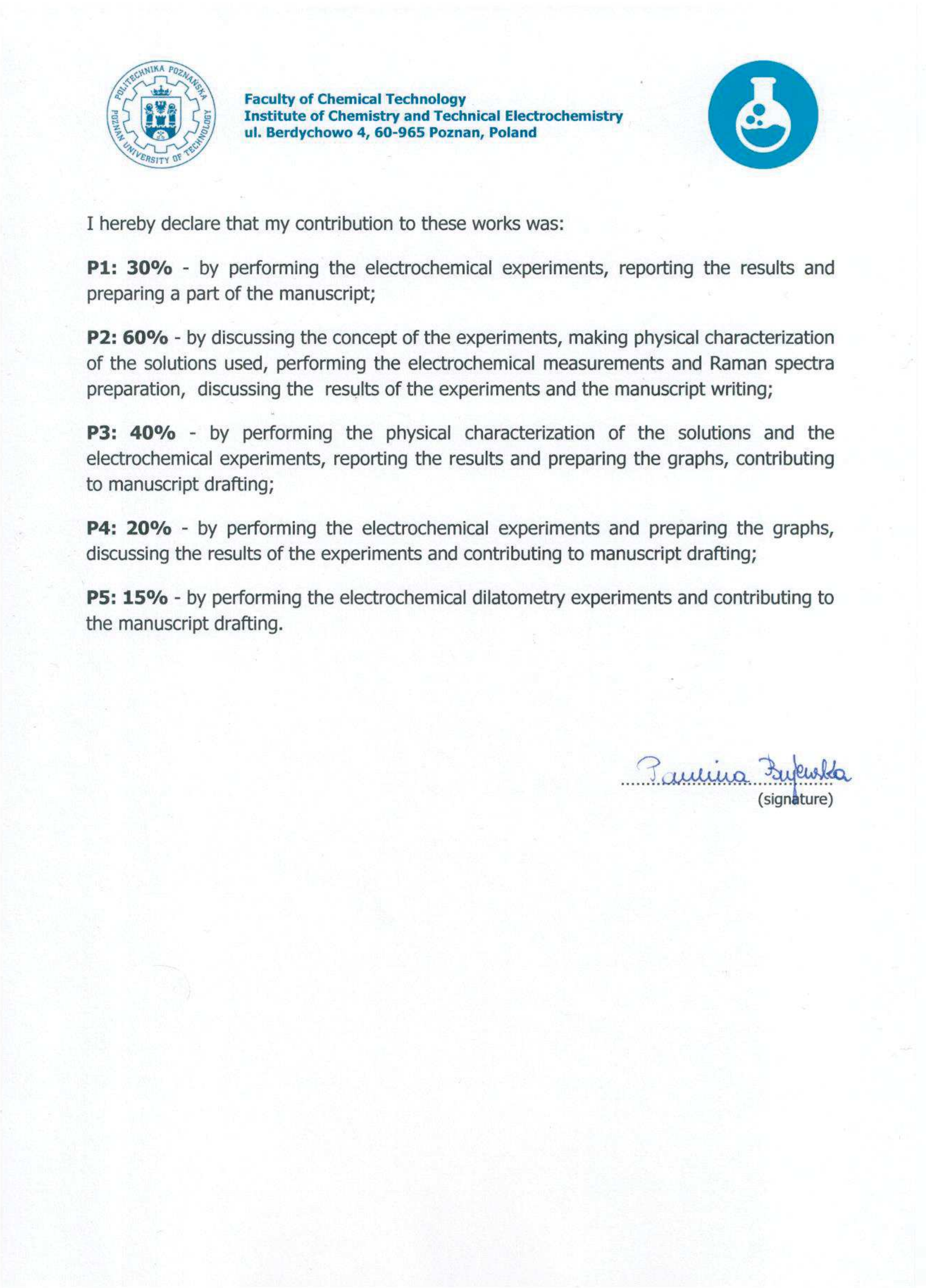
P1. Barbara Gorska (30%), **Paulina Bujewska (30%)**, Krzysztof Fic (40%)
Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors
Physical Chemistry Chemical Physics 19 (2017) 7923-7935
DOI: 10.1039/C7CP00722A

P2. Paulina Bujewska (60%), Barbara Gorska (10%), Krzysztof Fic (30%)
Gold nanoparticles for power retention in electrochemical capacitors with KSCN-based aqueous electrolyte
Journal of Power Sources Advances 14 (2022) 100087
DOI: 10.1016/j.powera.2022.100087

P3. Paulina Bujewska (40%), Barbara Gorska (30%), Krzysztof Fic (30%)
Redox activity of selenocyanate anion in electrochemical capacitor application
Synthetic Metals 253 (2019) 62-72
DOI: 10.1016/j.synthmet.2019.04.024

P4. Krzysztof Fic (25%), Barbara Gorska (25%), **Paulina Bujewska (20%)**, François Béguin (20%), Elzbieta Frackowiak (10%)
Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors
Electrochimica Acta 314 (2019) 1-8
DOI: 10.1016/j.electacta.2019.04.161

P5. Przemyslaw Galek (30%), **Paulina Bujewska (15%)**, Scott Donne (5%), Krzysztof Fic (10%), Jakub Menzel (40%)
New insight into ion dynamics in nanoporous carbon materials: An application of the step potential electrochemical spectroscopy (SPECS) technique and electrochemical dilatometry
Electrochimica Acta 377 (2021) 138115
DOI: 10.1016/j.electacta.2021.138115



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I hereby declare that my contribution to these works was:

P1: 30% - by performing the electrochemical experiments, reporting the results and preparing a part of the manuscript;

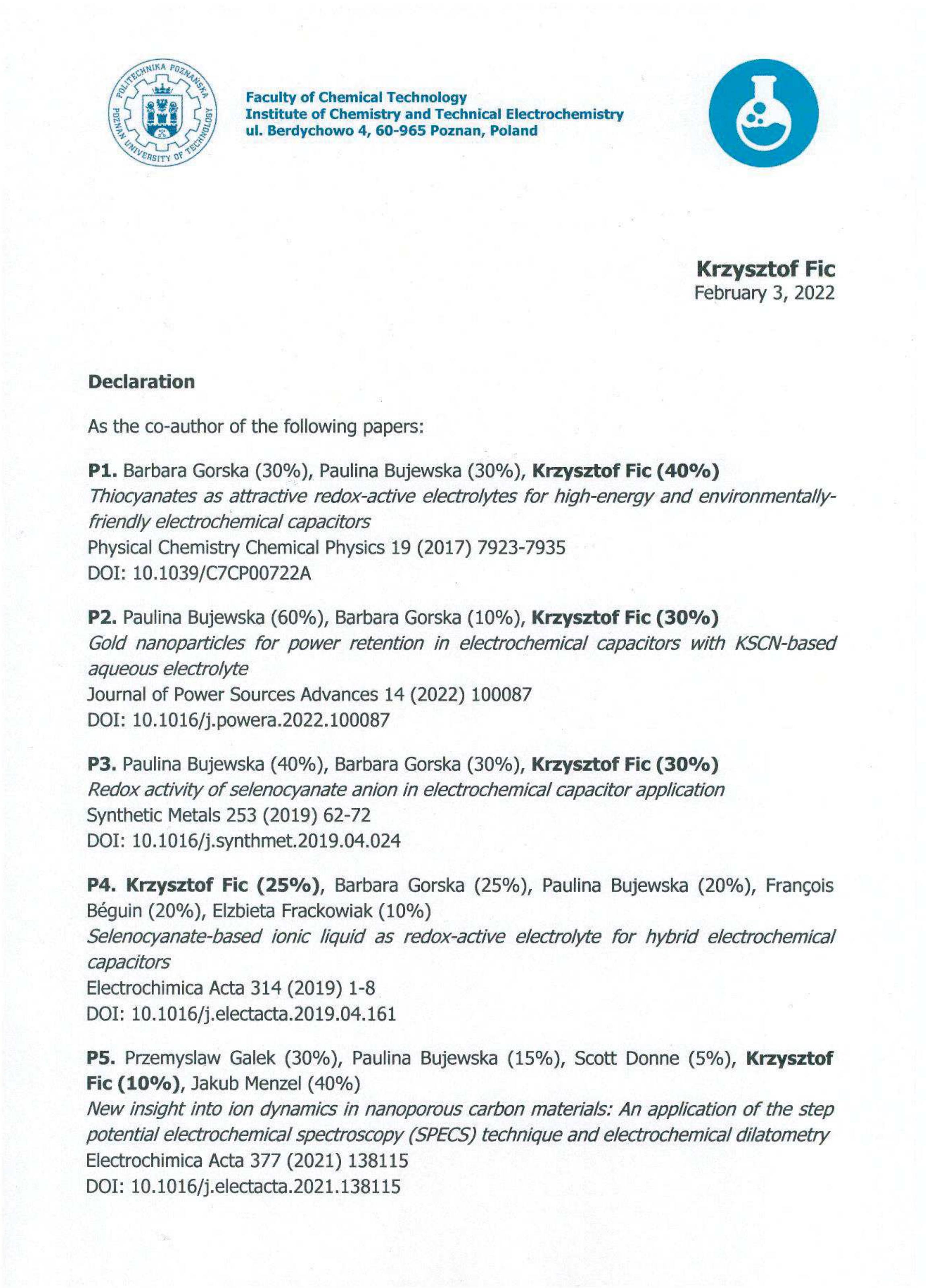
P2: 60% - by discussing the concept of the experiments, making physical characterization of the solutions used, performing the electrochemical measurements and Raman spectra preparation, discussing the results of the experiments and the manuscript writing;

P3: 40% - by performing the physical characterization of the solutions and the electrochemical experiments, reporting the results and preparing the graphs, contributing to manuscript drafting;

P4: 20% - by performing the electrochemical experiments and preparing the graphs, discussing the results of the experiments and contributing to manuscript drafting;

P5: 15% - by performing the electrochemical dilatometry experiments and contributing to the manuscript drafting.

Paulina Bujewska
(signature)



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Krzysztof Fic
February 3, 2022

Declaration

As the co-author of the following papers:

P1. Barbara Gorska (30%), Paulina Bujewska (30%), **Krzysztof Fic (40%)**
Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors
Physical Chemistry Chemical Physics 19 (2017) 7923-7935
DOI: 10.1039/C7CP00722A

P2. Paulina Bujewska (60%), Barbara Gorska (10%), **Krzysztof Fic (30%)**
Gold nanoparticles for power retention in electrochemical capacitors with KSCN-based aqueous electrolyte
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DOI: 10.1016/j.powera.2022.100087

P3. Paulina Bujewska (40%), Barbara Gorska (30%), **Krzysztof Fic (30%)**
Redox activity of selenocyanate anion in electrochemical capacitor application
Synthetic Metals 253 (2019) 62-72
DOI: 10.1016/j.synthmet.2019.04.024

P4. Krzysztof Fic (25%), Barbara Gorska (25%), Paulina Bujewska (20%), François Béguin (20%), Elzbieta Frackowiak (10%)
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Electrochimica Acta 314 (2019) 1-8
DOI: 10.1016/j.electacta.2019.04.161

P5. Przemyslaw Galek (30%), Paulina Bujewska (15%), Scott Donne (5%), **Krzysztof Fic (10%)**, Jakub Menzel (40%)
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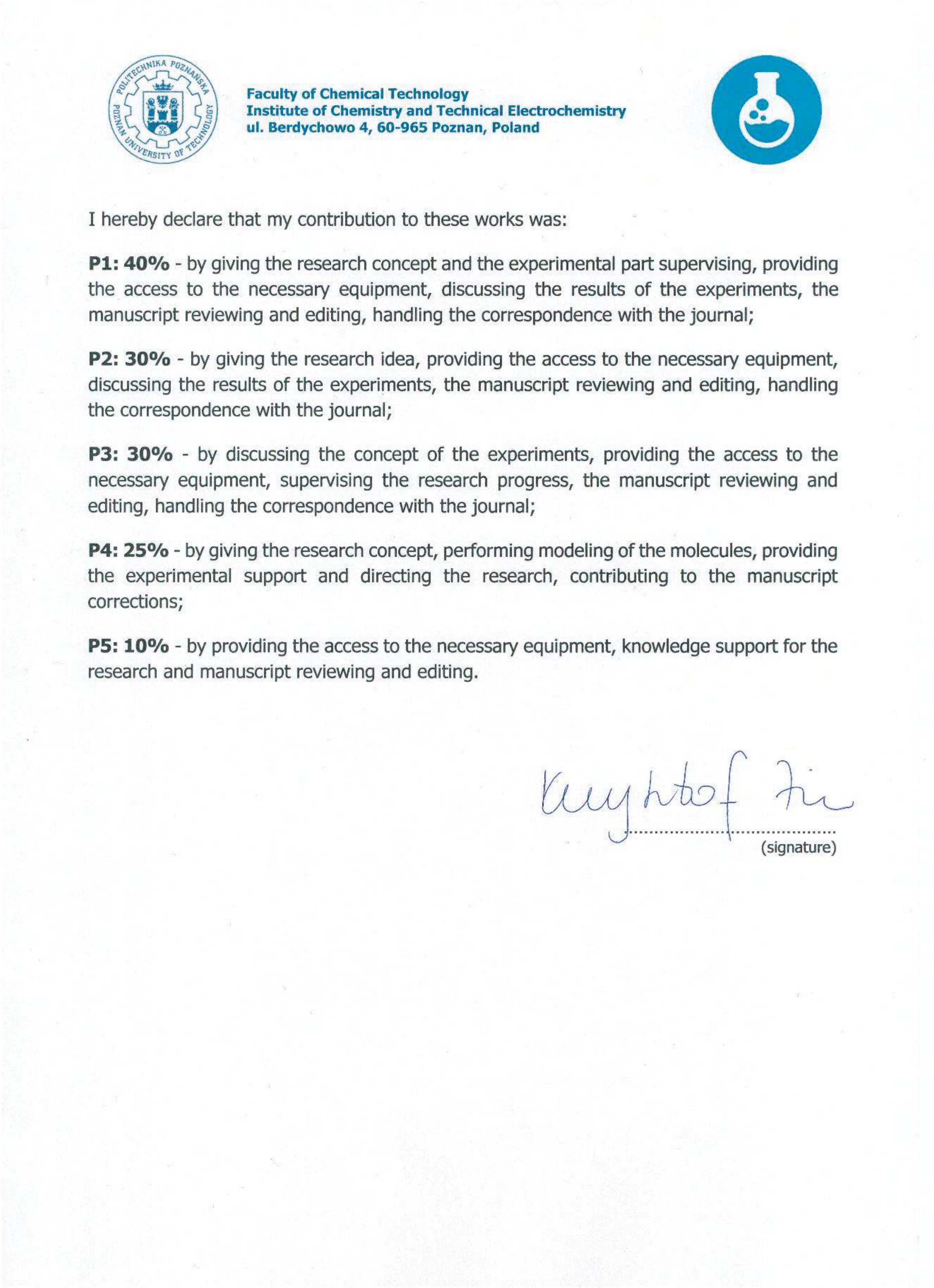
Electrochimica Acta 377 (2021) 138115
DOI: 10.1016/j.electacta.2021.138115



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I hereby declare that my contribution to these works was:

P1: 40% - by giving the research concept and the experimental part supervising, providing the access to the necessary equipment, discussing the results of the experiments, the manuscript reviewing and editing, handling the correspondence with the journal;

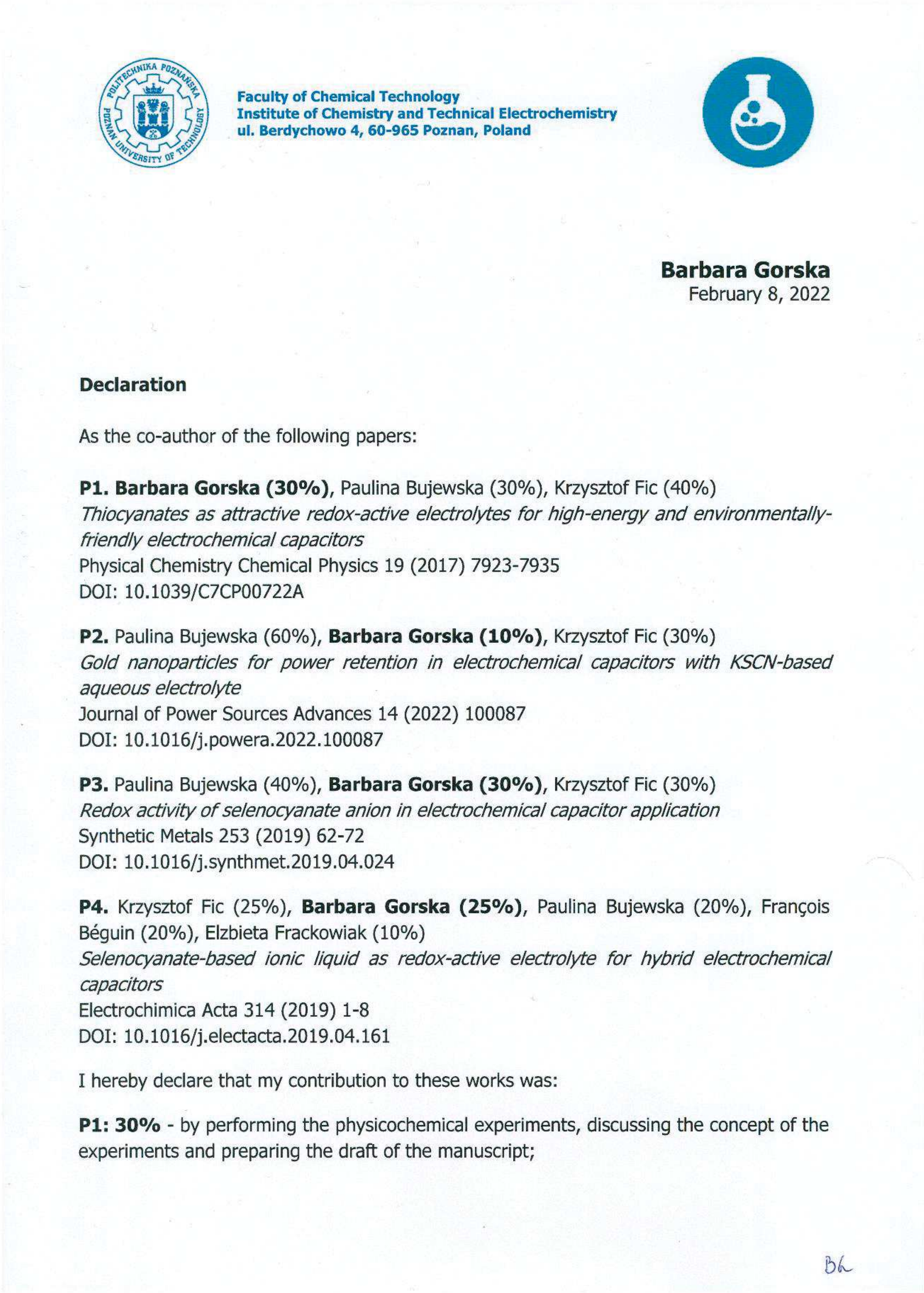
P2: 30% - by giving the research idea, providing the access to the necessary equipment, discussing the results of the experiments, the manuscript reviewing and editing, handling the correspondence with the journal;

P3: 30% - by discussing the concept of the experiments, providing the access to the necessary equipment, supervising the research progress, the manuscript reviewing and editing, handling the correspondence with the journal;

P4: 25% - by giving the research concept, performing modeling of the molecules, providing the experimental support and directing the research, contributing to the manuscript corrections;

P5: 10% - by providing the access to the necessary equipment, knowledge support for the research and manuscript reviewing and editing.

Krzysztof Fic
(signature)



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Barbara Gorska
February 8, 2022

Declaration

As the co-author of the following papers:

P1. Barbara Gorska (30%), Paulina Bujewska (30%), Krzysztof Fic (40%)
Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors
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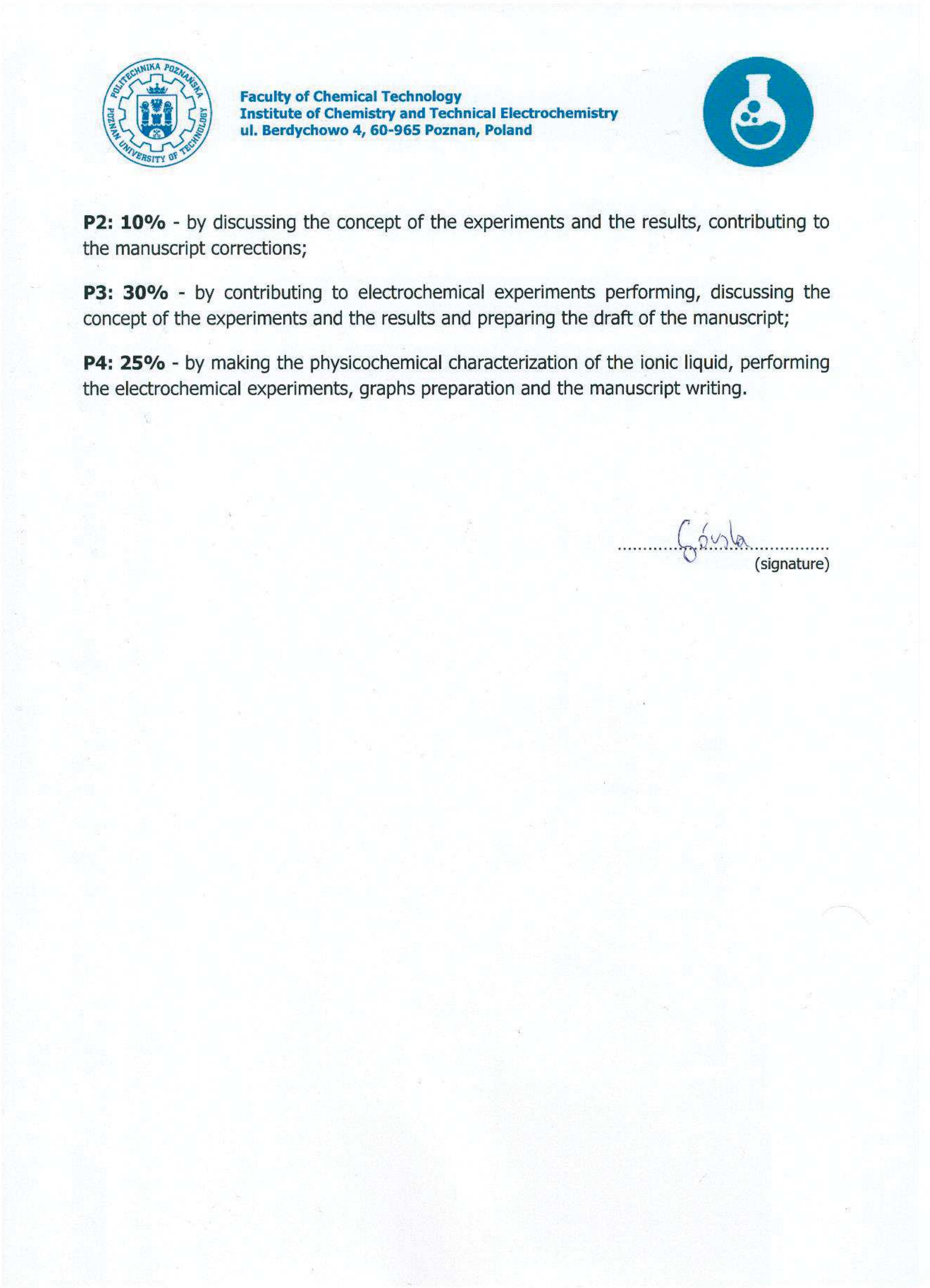
Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors
Electrochimica Acta 314 (2019) 1-8
DOI: 10.1016/j.electacta.2019.04.161

I hereby declare that my contribution to these works was:

P1: 30% - by performing the physicochemical experiments, discussing the concept of the experiments and preparing the draft of the manuscript;

BG



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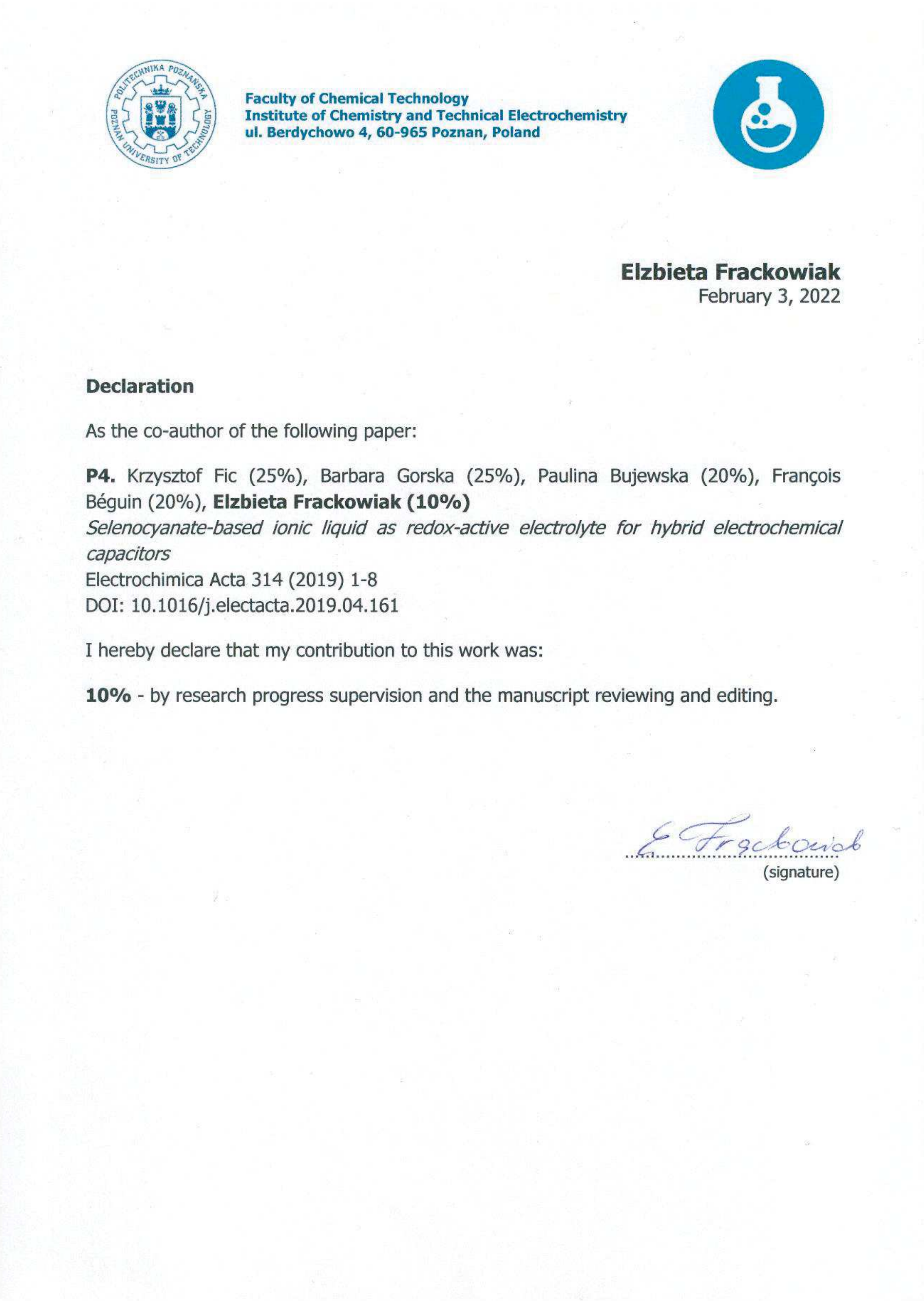
P2: 10% - by discussing the concept of the experiments and the results, contributing to the manuscript corrections;

P3: 30% - by contributing to electrochemical experiments performing, discussing the concept of the experiments and the results and preparing the draft of the manuscript;

P4: 25% - by making the physicochemical characterization of the ionic liquid, performing the electrochemical experiments, graphs preparation and the manuscript writing.

Górska
(signature)



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Elzbieta Frackowiak
February 3, 2022

Declaration

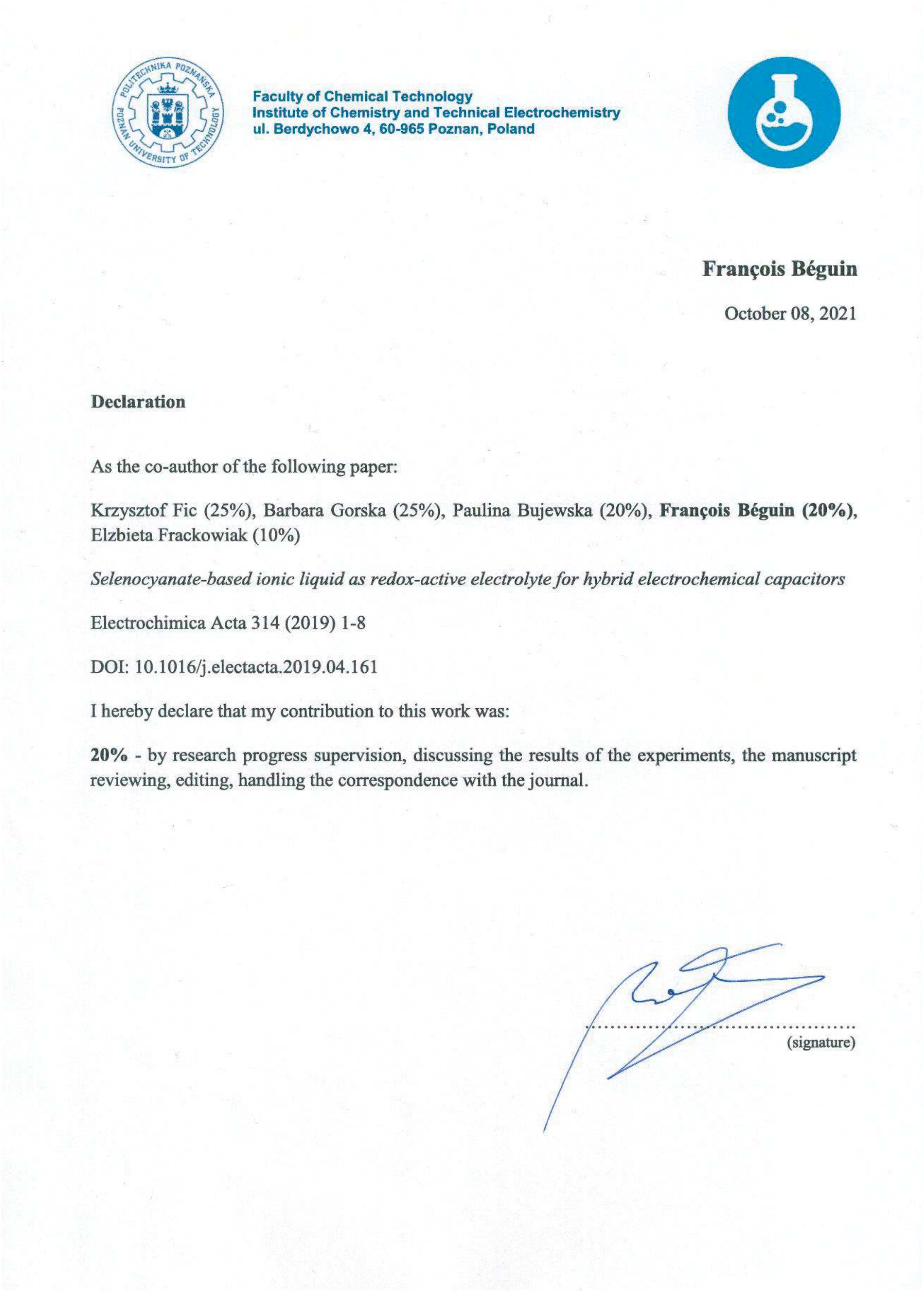
As the co-author of the following paper:

P4. Krzysztof Fic (25%), Barbara Gorska (25%), Paulina Bujewska (20%), François Béguin (20%), **Elzbieta Frackowiak (10%)**
Selenocyanate-based ionic liquid as redox-active electrolyte for hybrid electrochemical capacitors
Electrochimica Acta 314 (2019) 1-8
DOI: 10.1016/j.electacta.2019.04.161

I hereby declare that my contribution to this work was:

10% - by research progress supervision and the manuscript reviewing and editing.

E. Frackowiak
(signature)



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François Béguin

October 08, 2021

Declaration

As the co-author of the following paper:

Krzysztof Fic (25%), Barbara Gorska (25%), Paulina Bujewska (20%), **François Béguin (20%)**, Elzbieta Frackowiak (10%)

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I hereby declare that my contribution to this work was:

20% - by research progress supervision, discussing the results of the experiments, the manuscript reviewing, editing, handling the correspondence with the journal.

....
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THE UNIVERSITY OF
NEWCASTLE
AUSTRALIA

Professor Scott W. Donne
Discipline of Chemistry

February 9, 2022

Declaration

To whom it may concern,

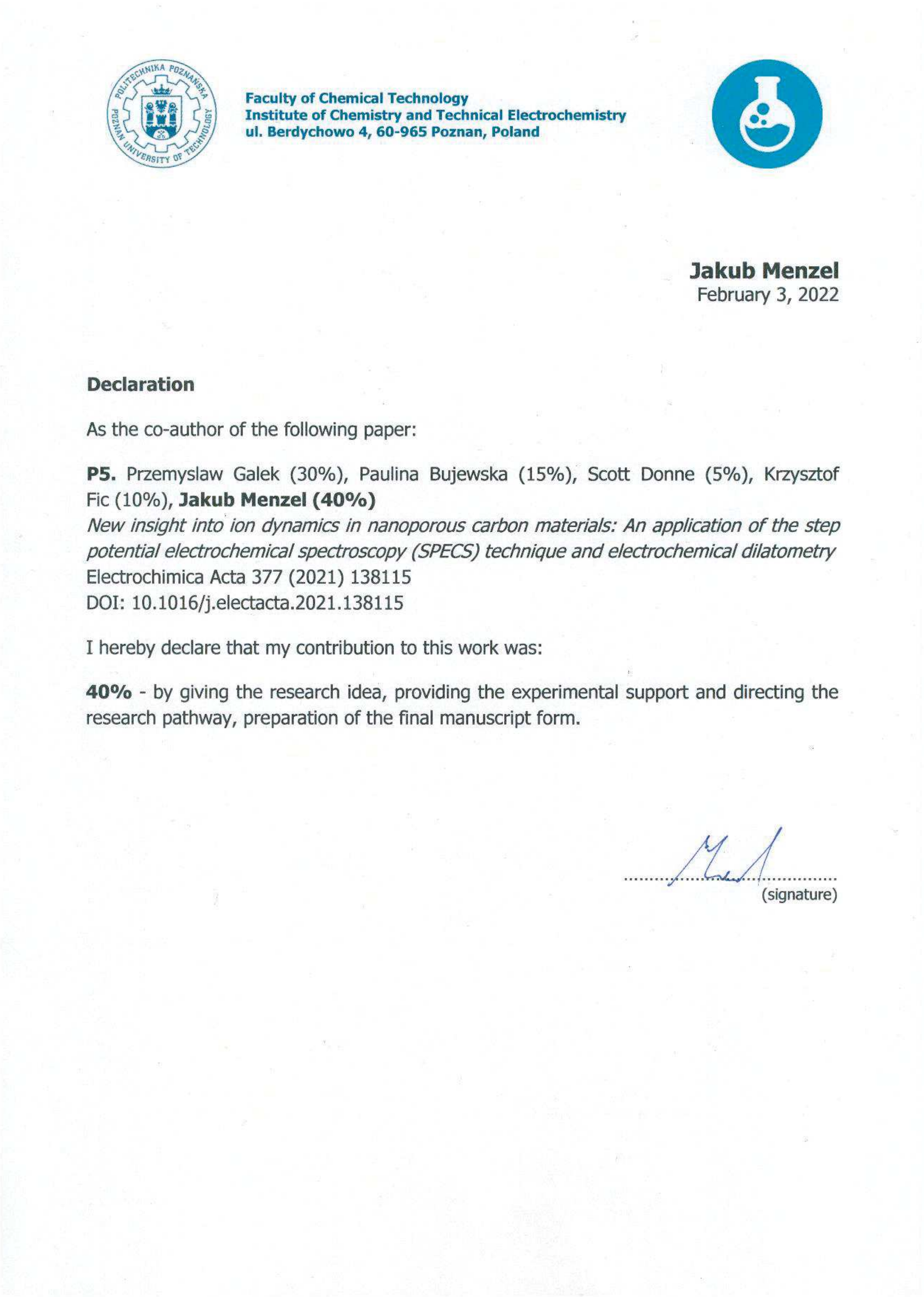
As the co-author of the following paper:

P5. Przemyslaw Galek (30%), Paulina Bujewska (15%), **Scott Donne (5%)**, Krzysztof Fic (10%), Jakub Menzel (40%)
New insight into ion dynamics in nanoporous carbon materials: An application of the step potential electrochemical spectroscopy (SPECS) technique and electrochemical dilatometry
Electrochimica Acta 377 (2021) 138115
DOI: 10.1016/j.electacta.2021.138115

I hereby declare that my contribution to this work was:
5% - by providing the research support (verification of the calculation results, discussions) concerning the SPECS calculations.

Yours sincerely,

Scott W. Donne



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Jakub Menzel
February 3, 2022

Declaration

As the co-author of the following paper:

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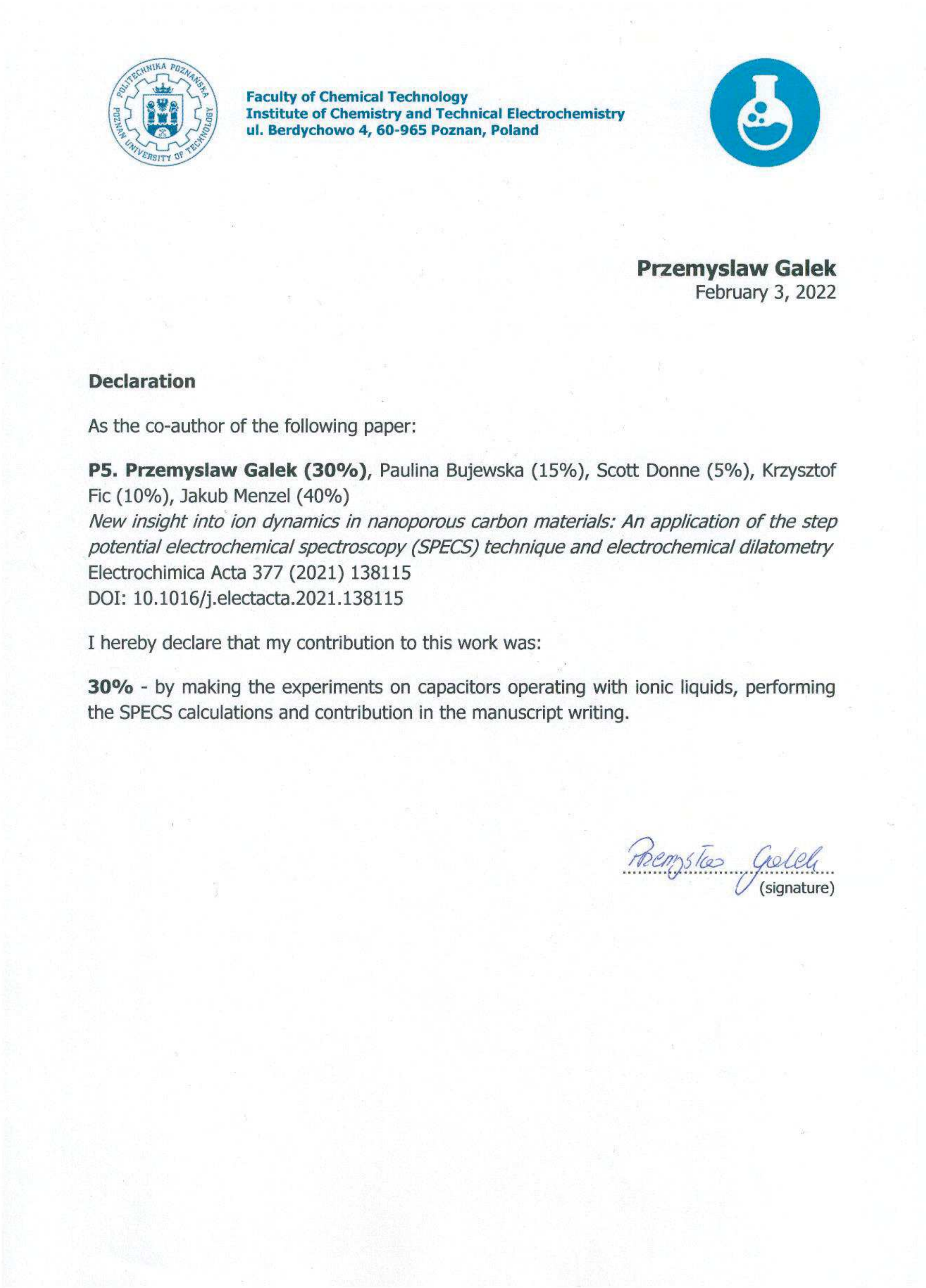
I hereby declare that my contribution to this work was:

40% - by giving the research idea, providing the experimental support and directing the research pathway, preparation of the final manuscript form.

....
(signature)



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Przemyslaw Galek
February 3, 2022

Declaration

As the co-author of the following paper:

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I hereby declare that my contribution to this work was:

30% - by making the experiments on capacitors operating with ionic liquids, performing the SPECS calculations and contribution in the manuscript writing.

Przemysław Galek
(signature)

PUBLICATIONS

P1

Górska B., Bujewska P., Fic K.

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