

γ -Valerolactone as Sustainable and Low-Toxic Solvent for Electrical Double Layer Capacitors

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In this work, γ -valerolactone (GVL), a green solvent based on largely available biomass (carbohydrates), highly biodegradable, and with low eco-toxicological profile, was used as electrolyte component in energy storage devices. This solvent allowed the realization of electrolytes with good transport properties and high thermal stability, which could be successfully applied in electrical double layer capacitors (EDLCs). GVL-based EDLCs

could operate at 2.7–2.9 V and displayed good performance in term of capacitance, cycling stability, as well as specific energy and power. The results of this study indicate that the use of solvent obtained from largely available natural sources is a feasible strategy for the realization of sustainable and safe electrolytes for EDLCs.

Introduction

The energy production from renewable and sustainable sources is nowadays prioritized and considered as a challenging task in our society. For an effective introduction of these sources in our daily life, the use of efficient energy storage devices is mandatory.^[1] In the last years, enormous efforts have been made toward the development of different energy storage systems.^[2] Among the various electrochemical energy storage devices, supercapacitors or electrical double layer capacitors (EDLCs) are currently considered as one of the most important. In EDLCs, the energy is stored electrostatically through the formation of an electrical double layer at the electrode–electrolyte interface. Due to this storage process, these devices display high specific power (up to 10 kW kg⁻¹), extraordinary high cycle life (> 1 million cycles) and a very short charging/discharging time (seconds or less). However, they have a rather limited specific energy (5–8 Wh kg⁻¹).^[3] Due to these characteristics,

EDLCs are currently preferred for many applications in grid and transportation, which require a rapid energy delivery.^[4] The electrode active material utilized in commercial EDLCs is typically activated carbon (AC), while the electrolyte consists of an ammonium-based salt, for example tetraethylammonium tetrafluoroborate (Et₄NBF₄) dissolved in an organic solvent, such as acetonitrile (ACN) or propylene carbonate (PC).^[5] This electrode–electrolyte combination assures the realization of devices having an operating voltage in the order of 2.8–3.0 V, and displaying the above-mentioned properties.^[6]

It is evident that to achieve a sustainable use of energy, energy storage devices need to be also realized in a sustainable manner. Correspondingly, electrode materials (active and inactive) for EDLCs derived from natural sources have been intensively investigated in the last years. Several types of natural precursors and synthetic strategies have been proposed for the realization of carbonaceous materials that are suitable in EDLC applications.^[7] The results of these studies indicated that the synthesis of electrode materials from sustainable feedstocks is possible and that the use of these materials is able to guarantee a comparable cell performance to that of the conventional ones. On the other hand, very few works have thoroughly considered the investigation of sustainable electrolyte components in EDLC applications, although potential sustainable solvents have been mentioned in the literature.^[8] This difference represents a serious drawback for the development of sustainable EDLCs. As a matter of fact, ACN and PC are synthesized through well-established industrial processes, which are utilizing fossil-based sources as well as non-sustainable materials. Additionally, ACN is a toxic and highly flammable compound, while PC has recently shown some concerns about the penetration of the blood–cerebrospinal barrier.^[3a,5a,9] Taking these points into account, the introduction of less toxic, less flammable, and more sustainable electrolytes is urgently needed for the development of sustainable EDLCs.


In this study, we report the use of the bio-based solvent γ -valerolactone (GVL) as electrolyte component for EDLCs. GVL is obtained from biomass, and has a low eco-toxicological profile,


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good biodegradability, and low flammability.^[10] This solvent has been indicated as an interesting candidate in view of the development of innovative and sustainable electrolytes.^[8c] Nevertheless, its use in EDLC has not been considered so far. Initially the chemical-physical properties of GVL-based electrolytes are investigated with different conducting salts and concentrations. Afterwards, the use of these electrolytes in EDLCs is considered, and their impact on the electrochemical performance of these devices is analyzed in detail. The aim of this work is to supply a proof of concept about the possibility to realize sustainable and safe solvents for EDLCs.

Results and Discussion

GVL versus conventional solvents for EDLC electrolytes

The use of solvents that can guarantee a large temperature range of use and, at the same time, are displaying low flammability and low toxicity is extremely important for the development of advanced EDLCs.^[3a,5a] GVL exhibits a low melting point of -30°C and a high boiling point of 207°C , which can provide a broad temperature range for EDLC applications. Besides, it has a high flash point of 96°C , which ensures low flammability.^[10] Furthermore, very importantly, it shows a low eco-toxicological profile with a Lethal Dose 50% (LD_{50}) of 8800 mg kg^{-1} (oral for rat).^[10] Additionally, the price of GVL is comparable to that of ACN and PC. These properties make GVL an interesting solvent for EDLCs, as it is also evident when the properties of this solvent are compared with those of the state-of-the-art solvents of this technology (see Table 1).

From a point of view of feedstock precursors, the synthesis of ACN and PC starts from fossil-based compounds. ACN is a side product of the SOHIO process for the synthesis of acrylonitrile starting from propylene, ammonia, and oxygen. This process uses bismuth phosphomolybdate as catalyst in harsh condition ($400\text{--}500^{\circ}\text{C}$, $50\text{--}200\text{ kPa}$), an aqueous bath of sulfuric acid to neutralize the excess of ammonia, and a distillation process to separate acrylonitrile from side products.^[13] From a practical point of view, this condition made this compound problematic even for the supply chain, and has already caused a shortage in 2008.^[14] PC is mainly produced by

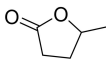
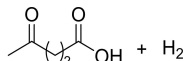
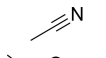
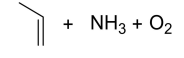
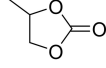
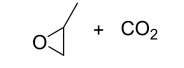
the addition of CO_2 to propylene oxide, which has also a high risk-profile (acute tox. 3 dermal, acute tox. 3 inhalation, acute tox. 4 oral; carc. 1B; eye irrit. 2; flam. liq. 1; muta. 1B). This process has a good efficiency in terms of atom economy and E-factor but needs high-purity reagents (epoxides) and severe conditions ($105\text{--}200^{\circ}\text{C}$, $3450\text{--}6900\text{ kPa}$).^[15]

As mentioned in the Introduction, the realization of sustainable electrolyte components is fundamental importance for the development of EDLCs. To reach this goal, one of the most important pre-requirements is the possibility to utilize abundant and renewable precursors (e.g., biomass) and to design sustainable chemical pathway for the synthesis of the solvent of these devices. So far, nonetheless, this aspect has only been marginally considered, and only few studies have been dedicated to the synthesis of sustainable solvents.^[8a] Beside the favorable properties of GVL, its production also meets the main sustainability aspect. Indeed, it can be produced by hydrogenation and dehydration starting from levulinic acid (Scheme 1), which is itself one of the most relevant biobased chemical platforms. Several research groups have focused on improving its production conditions, using heterogeneous non-precious metal catalysts and hydrogen donor compounds (e.g., formic acid, methanol, ethanol, 2-propanol) to avoid a high-pressure hydrogen atmosphere.^[16] Within this context, the development of innovative and high-value applications of GVL represents a driving-force to stimulate its industrial production.

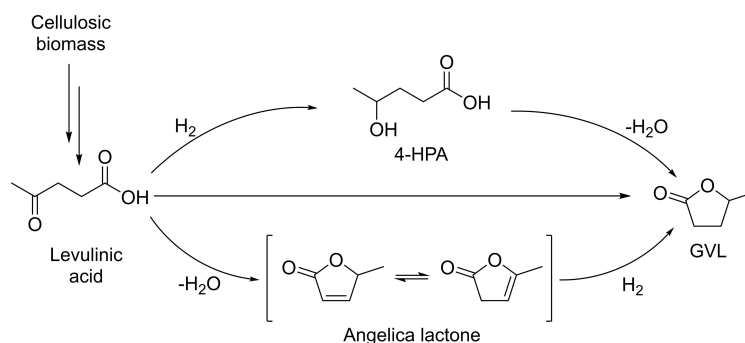
Chemical-physical characterization of GVL-based electrolytes

GVL has been utilized for the realization of electrolytic solutions suitable for EDLCs. Initially, the solubility of two conducting salts, the state-of-the-art Et_4NBF_4 and the alternative 1-methyl-1-butylpyrrolidinium tetrafluoroborate ($\text{Pyr}_{14}\text{BF}_4$) in GVL, has been considered. It has been found that at room temperature the maximum concentration of Et_4NBF_4 that can be dissolved in GVL is 0.6 M . The solubility of $\text{Pyr}_{14}\text{BF}_4$ in GVL is higher, and using this salt it is possible to realize an electrolytic solution with a concentration equal to 1 M . Therefore, we decided to investigate three GVL-based electrolytes, namely $0.6\text{ M Et}_4\text{NBF}_4$ in GVL, $0.6\text{ M Pyr}_{14}\text{BF}_4$ in GVL, and $1\text{ M Pyr}_{14}\text{BF}_4$ in GVL. These

Table 1. Comparison of important properties of the solvents GVL, ACN, and PC for the use in EDLCs, taken from the literature.^[8b,10,11]

Solvent	Melting point [°C]	Boiling point [°C]	Flash point [°C]	Dielectric constant (25 °C)	LD_{50} oral, rat [mg kg^{-1}]	Price quotation ^[a] [€ kg^{-1}]	Chemical structure	Precursors
GVL	-31	207	96	34	8800	65.6		
ACN	-48	81	2	36	2460	141.8		
PC	-49	242	132	65	34600	98.0		

[a] Price quotation for 10 kg (or 10 L) with purity $\geq 99\%$; for PC the quotation refers to 2 L of product (10 kg or 10 L quotation not available), estimated based on Ref. [12].



Scheme 1. GVL synthetic pathway. 4-HPA = 4-hydroxypentanoic acid.

electrolytes have been selected to gain information about the influence of the nature and concentration of the salts on the electrolyte's properties.

Figure 1 shows a comparison of some chemical-physical properties as well as electrochemical stability window (ESW) of the investigated GVL-based electrolytes. Figure 1a,b presents the comparison of the conductivity as well as viscosity of the electrolytes in the temperature range of -30 to 80 °C. As shown in Figure 1a, at 20 °C 0.6 M Et_4NBF_4 in GVL displays a

conductivity of 7.3 mS cm^{-1} , which is higher with respect to that of 0.6 M $\text{Pyr}_{14}\text{BF}_4$ in GVL (5.4 mS cm^{-1}). These values are lower than that displayed by conventional electrolytes, for example 1 M Et_4NBF_4 in PC that displays a conductivity of 13 mS cm^{-1} at 20 °C.^[17] The lower salt concentration of the GVL-based electrolytes is very likely the main reason of this difference. This hypothesis is also supported by the fact that at 20 °C the electrolyte 1 M $\text{Pyr}_{14}\text{BF}_4$ in GVL displays a conductivity of 9.0 mS cm^{-1} . Notably, this latter value is very similar to that

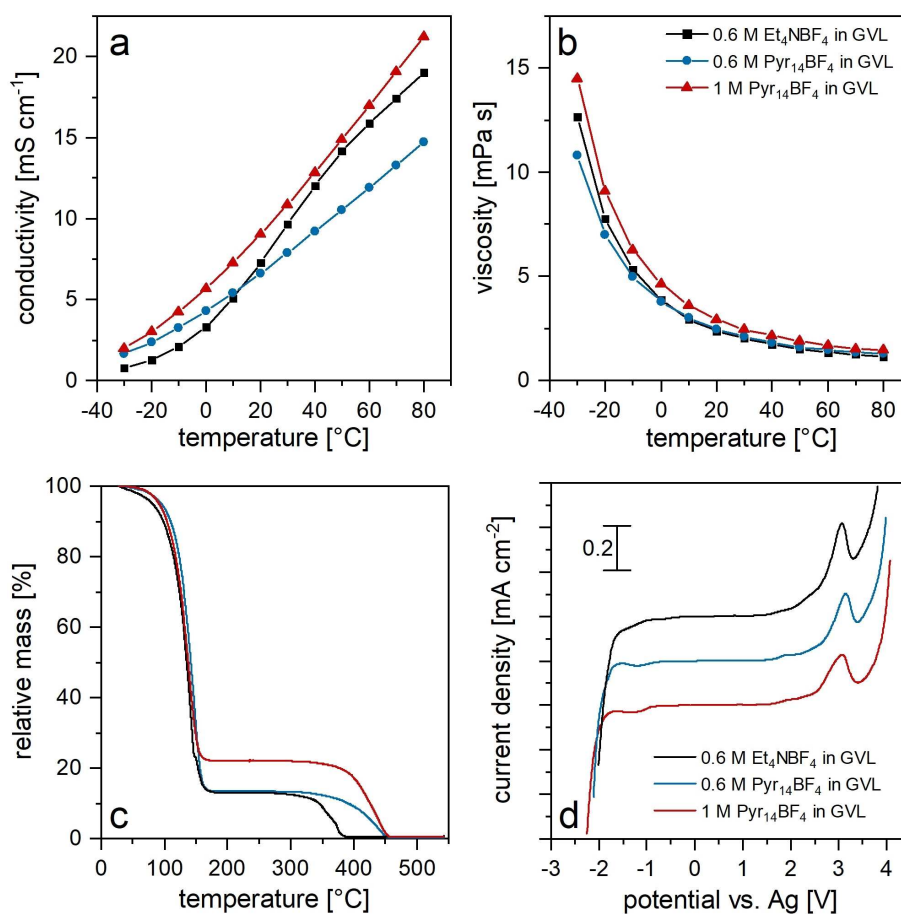


Figure 1. Comparison of (a) conductivity, (b) viscosity in the temperature range from -30 to 80 °C, (c) thermal stability in a temperature range from 30 to 550 °C, and (d) ESW of the electrolytes 0.6 M Et_4NBF_4 in GVL, 0.6 M $\text{Pyr}_{14}\text{BF}_4$ in GVL, and 1 M $\text{Pyr}_{14}\text{BF}_4$ in GVL.

displayed by the electrolyte 1 M Pyr₁₄BF₄ in PC (9.5 mS cm⁻¹).^[17] Throughout the entire investigated temperature range, 0.6 M Et₄NBF₄ in GVL presents a different conductivity trend compared to that shown by the electrolytes containing Pyr₁₄BF₄. A possible explanation for this behavior can be different interactions between different salts and the solvent, whereby the salt Et₄NBF₄ in GVL tends to form ion pairs more easily at lower temperatures (< 0 °C) in comparison to the electrolytes containing Pyr₁₄BF₄, resulting in the lowest conductivities. As presented in Figure 1b, at 20 °C the viscosity of 0.6 M Et₄NBF₄ in GVL (2.0 mPas) is comparable to that of 0.6 M Pyr₁₄BF₄ in GVL (2.1 mPas). In contrast to that, 1 M Pyr₁₄BF₄ in GVL displays a slightly higher viscosity of 2.5 mPas. These values of viscosity are very comparable to that reported for PC-based electrolytes containing the same salts.^[5a] The thermal behavior of the GVL-based electrolytes is illustrated in Figure 1c. During the thermal ramp measurement from 30–550 °C, all electrolytes display a gradual decrease in mass from 30–100 °C because of the evaporation of the solvent GVL. These results are showing that the GVL-based electrolytes have lower volatility compared to the conventional ACN-based electrolytes, which generally present a rapid mass loss with the increase in temperature.^[18] As the temperature is further increased, a rapid mass loss of the GVL-based electrolytes is observed until the evaporation ends at around 170 °C. After that, there is no significant change in the electrolyte mass, indicating that the component left in the electrolytes, which is the corresponding conducting salts, remains stable in the following temperature range. At the points in which the electrolyte mass has decreased to zero, the respective conducting salt as well as GVL in the electrolytes have fully decomposed. Due to the higher thermal stability of Pyr₁₄BF₄ compared to Et₄NBF₄, the temperature at which the electrolytes have decomposed completely is higher in the electrolytes containing the former than the latter salt (450 vs. 375 °C, respectively).^[19] Figure 1d compares the ESW of the GVL-based electrolytes. As seen, the electrolytes display an overall ESW larger than 4 V, which allows their application in EDLCs. Considering these results, all three electrolytes appear to have properties suitable for the use in EDLCs. Consequently, they have been investigated in combination with AC-electrodes in EDLCs.

Electrochemical performance of EDLCs containing GVL-based electrolytes

Initially, the maximum operating voltage achievable with the GVL-based electrolytes has been defined by utilizing cyclic voltammetry (CV) and setting the coulombic efficiency limit at 99%. The information about the cell setup is reported in the Experimental Section, and the CV curves are available in Figure S1 of the Supporting Information. The operating voltage of the devices containing 0.6 M Et₄NBF₄ in GVL is 2.7 V, while that of the devices containing 0.6 M Pyr₁₄BF₄ in GVL and 1 M Pyr₁₄BF₄ in GVL is 2.9 V. It is interesting to note that a change in conducting salt does not have a significant impact on the operating voltage of the GVL-based electrolytes. This is not the

case when different solvents, for example PC, are used.^[20] Besides, the electrolyte concentration does not display a strong effect on improving the operating voltage of the GVL-based electrolytes. Overall, the operating voltage displayed by the GVL-based EDLCs is comparable to that achievable with the state-of-the-art electrolytes.^[20,21]

Figure 2a–c compares the CV profiles of the investigated GVL-based EDLCs. In order to have an easier comparison about the behavior of the devices, the EDLCs containing Et₄NBF₄ were tested by utilizing a maximum operating voltage of 2.7 V, while the operating voltage of the device containing Pyr₁₄BF₄ was 2.9 V. As shown, all EDLCs display the typical rectangular CV profile, indicating the capacitive behavior of EDLCs containing the GVL-based electrolytes. It has to be mentioned that,

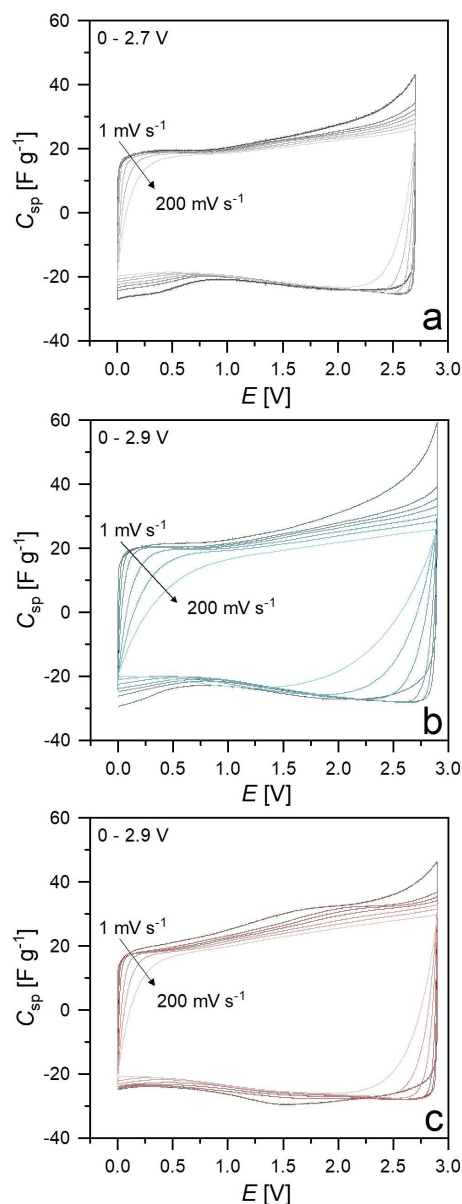


Figure 2. CVs of the investigated EDLCs using the electrolytes (a) 0.6 M Et₄NBF₄ in GVL, (b) 0.6 M Pyr₁₄BF₄ in GVL, and (c) 1 M Pyr₁₄BF₄ in GVL with the scan rates ranging from 1–200 mV s⁻¹.

however, there is the presence of some peaks at 1 mVs^{-1} , which is possibly caused by the occurrence of side reactions taking place between the electrode surface and the electrolytes. Moreover, a distortion of the rectangular CV profiles is noted with the increase in scan rates. The bigger distortion of the CV profiles is observed in the EDLCs containing $0.6 \text{ M Pyr}_{14}\text{BF}_4$ in GVL (Figure 2b), which is caused by the relatively poor transport properties of this electrolyte compared to that of the other two. The capacitance displayed by the devices, which is ranging between $20\text{--}25 \text{ Fg}^{-1}$, is comparable to that displayed by AC-based EDLCs containing conventional or different type of alternative electrolytes, as shown in Table S1 of the Supporting Information.^[17,20–22]

Figure 3a compares the capacitance retention of the investigated GVL-based EDLCs during galvanostatic charge–discharge carried out at current densities ranging from $0.5\text{--}20 \text{ Ag}^{-1}$. As shown, all the devices display good capacitance retention ($> 80\%$) up to 5 Ag^{-1} . Above this value of current density their behavior differentiates. The device containing $0.6 \text{ M Pyr}_{14}\text{BF}_4$ in GVL, which is the electrolyte with the lowest conductivity, loses most of its capacitance at 10 Ag^{-1} and at 20 Ag^{-1} is no longer able to provide any capacitance. The device containing $1 \text{ M Pyr}_{14}\text{BF}_4$ in GVL displays higher capacitance retention, and it is keeping large part of its capacitance at 10 Ag^{-1} , while at 20 Ag^{-1} it can deliver only half of its initial capacitance. The different behavior of these two devices is obviously related to the conductivity of the used electrolytes. Interestingly, the device that achieved the highest capacitance retention is the one containing $0.6 \text{ M Et}_4\text{NBF}_4$ in GVL. As shown in Figure 3a, this device can retain large part of its initial capacitance also at 20 Ag^{-1} . Since the conductivity of this electrolyte is lower than those of the two electrolytes containing $\text{Pyr}_{14}\text{BF}_4$, this result indicates that the nature of the conducting salt seems to have a strong effect on the performance of the devices. It is reasonable to suppose that also the properties of the used AC are influencing the behavior of the device (as shown for other alternative electrolytes).^[23] Never-

theless, although of importance, this aspect is out scope of this work, and it will not be further investigated. The different behavior of the devices is well visible on the Ragone plot reported in Figure 3b. Owing to the higher operating cell potential at 2.9 V and the relatively high specific capacitance values, the EDLC containing $1 \text{ M Pyr}_{14}\text{BF}_4$ in GVL is able to achieve the highest specific energy of $23\text{--}28 \text{ Whkg}^{-1}$ in the current density range from $0.5\text{--}2 \text{ Ag}^{-1}$, compared to that of the other two electrolytes. Despite of the operating voltage at 2.9 V , the EDLC containing $0.6 \text{ M Pyr}_{14}\text{BF}_4$ in GVL does not show significantly high specific energy due to relatively low values of specific capacitance. Over the whole current density range from $0.5\text{--}20 \text{ Ag}^{-1}$, the EDLC containing $0.6 \text{ M Et}_4\text{NBF}_4$ in GVL is the one delivering the best performance, and at 10 Ag^{-1} it delivers a specific energy and power of 15 Whkg^{-1} and 23 kWkg^{-1} , respectively. These values are comparable to those observed for lab-scale AC-based EDLCs containing ACN- and PC-based electrolytes.^[18,20]

In order to acquire information about the long-term stability of EDLCs using GVL-based electrolytes, float tests have been performed at a maximum cell potential of 2.7 V . As shown in Figure 4, the EDLCs containing $0.6 \text{ M Et}_4\text{NBF}_4$ in GVL and $0.6 \text{ M Pyr}_{14}\text{BF}_4$ in GVL display a comparable capacitance retention of 73% after 250 h of floating at 2.7 V , whereas the EDLC containing $1 \text{ M Pyr}_{14}\text{BF}_4$ in GVL shows a capacitance retention of nearly 60% , although it was the system for which a higher operating voltage was determined.

The results reported above are indicating that the GVL-based EDLCs investigated in this work, and especially the system containing $0.6 \text{ M Et}_4\text{NBF}_4$ in GVL, display promising performance. As a matter of fact, although their operating voltage is not higher than that of EDLCs containing conventional electrolytes, they show good specific energy as well as power and a promising long-term stability. This latter aspect is particularly interesting because the solvent utilized for the experiment (non-battery grade) is, for obvious reasons, not as

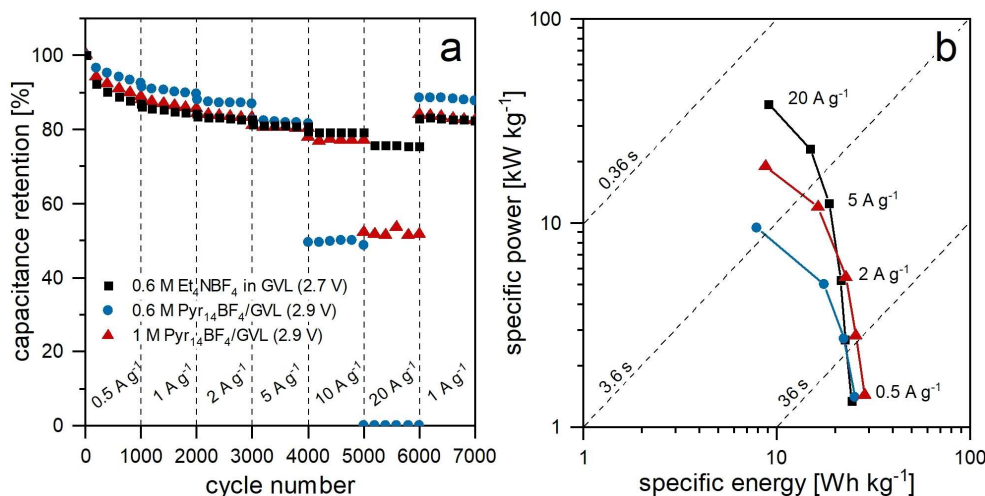


Figure 3. (a) Comparison of capacitance retention displayed by the GVL-based EDLCs at different current densities ranging from $0.5\text{--}20 \text{ Ag}^{-1}$ with the indicated respective cell voltage. (b) Comparison of specific power and energy in the Ragone plot for the corresponding investigated EDLCs.

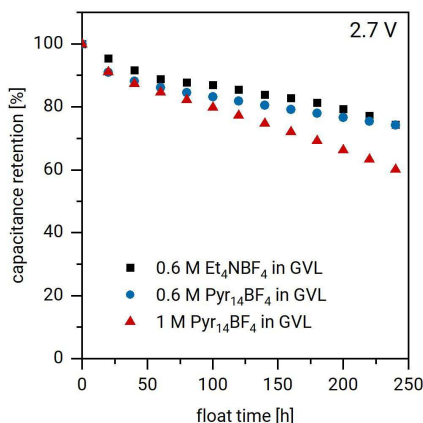


Figure 4. Comparison of capacitance retention displayed by the GVL-based EDLCs, which were investigated in a floating test of 250 h at the cell potential of 2.7 V.

pure as the ACN and PC utilized for the realization of the conventional electrolytes.

Post-mortem analysis for electrolyte degradation

To gain information about this important point, investigations on the electrolyte degradation taking place in GVL-based EDLCs by using post-mortem gas chromatography–mass spectrometry (GC-MS) analysis were performed. For this purpose, we carried out float tests at 2.7 and 2.9 V (for a total of 150 h) on devices containing the same electrodes and electrolytes discussed above but assembled in a modified cell setup (all details are reported in the Experimental Section). Based on the previous results, these tests have been carried out only on the EDLC containing 0.6 M Et₄NBF₄ in GVL. As shown in Figure 5, after 150 h floating at 2.7 V the device was able to retain 58% of its initial capacitance, while after the same floating time at 2.9 V its capacitance retention was 43%. As already discussed in our

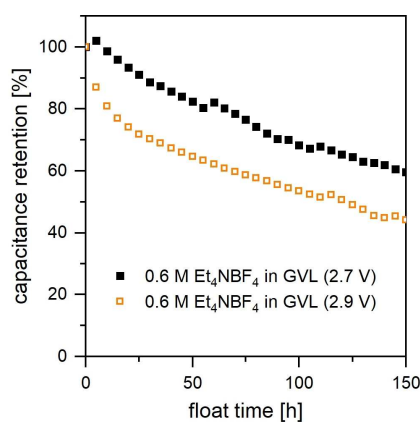


Figure 5. Comparison of capacitance retention displayed by GVL-based EDLCs in a modified cell setup, which were investigated in a floating test of 150 h at the cell potential of 2.7 and 2.9 V.

previous work, the lower stability observed on these experiments (compared to those reported above in Figure 4) is due to the used cell setup. Nevertheless, this latter modified cell setup is designed to investigate the electrolyte degradation, as it allows its extraction and its post-mortem analysis.^[18] Figure 6a compares the total ion chromatograms of 0.6 M Et₄NBF₄ in GVL after 150 h floating at 2.7 and 2.9 V with respect to the solvent GVL. The total ion chromatogram of GVL was obtained through GC-MS analysis to have an insight into its composition, as presented in Figure 6b. It is observed that the solvent GVL was detected at the retention time between 13.5–18.7 min. Besides, acetonitrile was also found in the sample because it has been utilized for cleaning purpose of the needle after every injection of the sample in the GC-MS device. From the measurements, it can be observed that there are different five-membered ring compounds detectable in the solvent, indicated by the peaks shown at the retention time starting from 19 min. These peaks are indicating the presence of some impurities in GVL. The peak at retention time of 31.8 min, which is assigned to the column bleeding, indicates that there is some loss of stationary phase from the column of the device (GC) into the sample. According to Figure 6a, the cells show a similar decomposition product at retention time of 5.2 min, which corresponds to the hydrogenated derivative of the solvent GVL, named as 2-methyloxolane or 2-methyltetrahydrofuran (2-MeTHF).^[24] Besides, despite of the increased capacitance loss during floating at 2.9 V, no additional decomposition products were detected in the electrolyte at this operating voltage (compared to the electrolyte during floating at 2.7 V). Taking into account that no significant decomposition products related to the conducting salts were detected, a possible explanation for the observed behavior might be that the degradation processes happened in the cell during floating are related to processes involving the solvent and possibly the electrode, which are occurring at both cell voltages. During floating at 2.9 V, however, this process has major effect in comparison to that at 2.7 V. Further studies are, however, certainly needed to better understand the dynamics of the degradation processes taking place in EDLCs containing GVL-based electrolytes.

Conclusion

The realization of sustainable electrical double layer capacitors (EDLCs) cannot be realized without the development of sustainable electrolytes. In this work, we demonstrated that γ -valerolactone (GVL), a biodegradable solvent from biomass with favorable eco-toxicological profile, can be successfully utilized for the realization of electrolytes suitable for EDLCs. We showed that GVL-based electrolytes exhibit good transport and thermal properties and that their use allows the realization of EDLCs with an operating voltage window of 2.7–2.9 V, which is comparable to that of conventional electrolytes. GVL-based EDLCs display good performance in term of capacitance, cycling stability, as well as specific energy and power (15 Wh kg⁻¹ and 23 kW kg⁻¹, respectively, at 10 A g⁻¹). In the future, it will be important to optimize the purification procedure to improve

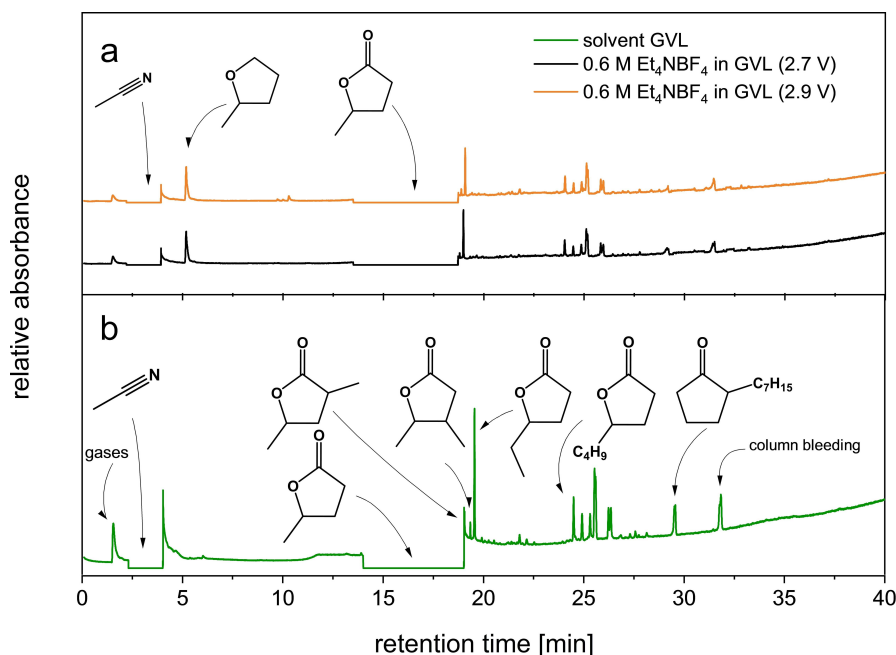


Figure 6. Comparison of total ion chromatograms of (a) the extracted electrolyte 0.6 M Et_4NBF_4 in GVL after being investigated in the modified cell setup through floating of 150 h at 2.7 and 2.9 V respectively with respect to (b) the solvent GVL.

the purity of GVL and to identify the best salt-solvent combination in order to further improve the performance of GVL-based EDLCs. Nonetheless, the results of this study clearly indicated that the use of solvent derived from largely available natural sources is a feasible strategy towards the goal of sustainable and safe electrolytes for EDLCs.

Experimental Section

Electrolyte preparation

The solvent GVL ($\geq 99\%$, Sigma-Aldrich) was dried over the molecular sieve (3 \AA) to reduce its water content below 25 ppm, which was confirmed using Karl-Fischer titration. The conducting salts Et_4NBF_4 (Sigma-Aldrich) and $\text{Pyr}_{14}\text{BF}_4$ (IoLiTec) were used in combination with GVL for the realization of the electrolytes investigated in this work.

Chemical and physical characterization

The conductivity was determined in the temperature range from -30 to 80°C utilizing a potentiostat (ModuLab XM ECS from Solartron Analytical). A conductivity cell, consisting of two parallel platinized platinum electrodes with a known cell constant, was utilized for the experiments. The measurements were carried out according to the procedure described in literature.^[25] Besides, the viscosity was measured over the same temperature range with a Modular Compact Rheometer MCR 102 (from Anton Paar RheoCompas) at the shear rate of 1000 s^{-1} , whereby 0.5 mL electrolyte sample was applied. The measurements were carried out according to the procedure described in literature.^[25]

The thermal stability of the electrolytes was investigated by carrying out thermogravimetric analysis (TGA) performed using a PerkinElmer STA 6000. Before starting the measurements, the device was purged with nitrogen gas for 1 h. The electrolyte samples were analyzed under nitrogen atmosphere with a gas flow of 20 mL min^{-1} and a gas pressure of 2.2 bar, whereby one sample ($\approx 10 \text{ mg}$) was pipetted into a platinum crucible and placed into the device. Thermal ramp measurements in the temperature range from 30 to 550°C , and with a heating rate of $10^\circ\text{C min}^{-1}$, were carried out.

Electrode preparation

Composite electrodes containing activated carbon (YP-80f, from Kuraray) as active material, carbon black (Super C65, from Imerys) as conducting agent, and sodium carboxymethyl cellulose (NaCMC2000, from Walocel) as binder, in the mass ratio of 90:5:5, were prepared according to the experimental procedure reported in Ref. [26]. AC electrodes with different thickness (80 , 100 , and $200 \mu\text{m}$) were made.^[27] The electrode area accounted for 1.13 cm^2 and the active mass loading was in the range of 1.7 – $4.7 \text{ mg per electrode}$, varying based on the electrode thickness.

Self-standing AC electrodes, which were required in the electrochemical characterization of the electrolytes, were prepared by mixing activated carbon (DLC Supra 50, Norit), carbon black (Super C65, from Imerys), and 60 wt% polytetrafluoroethylene (PTFE) suspension in water (from Sigma Aldrich) in the ratio of 85:10:5 with excess ethanol, following a procedure identical to that reported in Ref. [28]. The electrode area was 1.13 cm^2 , and the electrode mass loading was in the range of 35 – $45 \text{ mg per electrode}$.

Electrochemical measurements

All electrochemical tests have been carried out at room temperature using Swagelok-type cells in two- as well as three-electrodes configuration.^[29] They were assembled in argon-filled glovebox with water and oxygen content lower than 1 ppm. In each cell, a Whatman GF/D glass fiber filter (520 μm thickness) was used as separator, which was drenched with 120–150 μL electrolyte. All electrochemical investigations were performed at a BioLogic VMP-3 and an Arbin LBT21084 multichannel potentiostatic-galvanostatic system.

The electrochemical stability window of the electrolytes was determined in three-electrodes configuration through linear sweep voltammetry (LSV) by using a platinum disc as working electrode, a self-standing AC electrode as counter electrode, and silver wire as quasi-reference electrode. The investigations were carried out with a scan rate of 1 mVs^{-1} according to the procedure reported in Ref. [30].

The operating voltage range of the electrolytes was investigated in three-electrodes configuration, in which silver wire was applied as quasi-reference electrode. AC electrode was used as working electrode, while self-standing AC electrode was utilized as counter electrode. The positive and negative potential limits were determined separately in two cells through CV with a scan rate of 5 mVs^{-1} . The measurements were carried out using the setting described in Ref. [30]. The operating voltage range was selected at the potential limits where the coulombic efficiency decreased below 99%. The coulombic efficiency was obtained through dividing the area under the CV curve during discharging by the area under the CV curve during charging.

The electrochemical performance of the EDLCs containing the electrolytes were investigated by utilizing CV carried out at different scan rates (1, 5, 10, 20, 50, 100, and 200 mVs^{-1}) and galvanostatic charge-discharge (GCD) performed at different current densities (0.5, 1, 2, 5, 10, 20, and 1 Ag^{-1}). 10 CVs were carried out at every scan rate, while 1000 cycles were carried out at every current density. The specific energy (E_{max}) and power (P_{max}) of the devices were calculated using the following equations [Eqs. (1) and (2)]:

$$E_{\text{max}} [\text{Wh kg}^{-1}] = \int \frac{V \times I}{m_{\text{act}} \times 3600} dt_{\text{d}} \quad (1)$$

$$P_{\text{max}} [\text{kW kg}^{-1}] = \frac{V_{\text{max}} \times I}{m_{\text{act}} \times 1000} \quad (2)$$

where V is the measured discharging voltage [V], V_{max} is the maximum voltage during discharging [V], I is the current [A], m_{act} is the total mass of active materials in the investigated cell [kg], t_{d} is the discharging time [s], and a factor of 3600 is taken into account for the conversion of seconds into hours.

The long-term stability of the EDLCs was evaluated by carrying out float tests performed at 2.7 V for a total of 250 h. Every 20 h, 50 charge/discharge cycles were carried out at 1 Ag^{-1} between 0–2.7 V.

Post-mortem investigation for electrolytes

The degradation processes occurring on the electrolyte during the EDLCs test were investigated utilizing a X-type Swagelok cell, identical to that utilized by our group in a previous study.^[18] In this cell, a ring-shaped spacer (3 mm thickness) with a cutout at one side was used instead of the Whatman glass fiber separator.^[18] Through this cutout, a larger volume of electrolyte in 1.4 mL was

injected into the cell to provide enough electrolyte reservoir for the later degradation analysis. Float tests were performed using the modified cells at 2.7 and 2.9 V with a voltage hold of 5 h for a total of 150 h. After each voltage hold, 5 charge/discharge cycles were carried out at 1 Ag^{-1} between 0 V and the applied cell voltage. At the end of the float tests, the cell was opened in an argon-filled glovebox, and 300 μL electrolyte was extracted. The extracted electrolyte was then investigated by carrying out post-mortem GC-MS analysis, following the same procedure reported in the literature.^[18] The post-mortem GC-MS measurements were carried out utilizing an Agilent 7890B GC, equipped with an Agilent 7683 Series ALS, and an Agilent 5977 A MS (EI-MSD, single quadrupole). The set-up contains an Agilent HP-5 ms column (30 m, ID 250 μm , DF 1 μm , –60 to 325 $^{\circ}\text{C}$) in an oven set to a temperature range of 70–280 $^{\circ}\text{C}$, applying a temperature ramp of 10 $^{\circ}\text{Cmin}^{-1}$. The injection volume was set to 5 μL and the respective carrier-gas flow (He) was set to 1 mLmin^{-1} at a split ratio of 3:1. The obtained mass-spectra were compared to a NIST/EPA/NIH Mass Spectral Library (version 2.2, build June 10, 2014), with the determined analytes showing a match probability higher than 70% displayed in the respective total ion chromatograms (TICs). The TICs were subjected to background subtraction and baseline correction.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: capacitors · gamma-valerolactone · electrolytes · post-mortem analysis · sustainable solvents

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