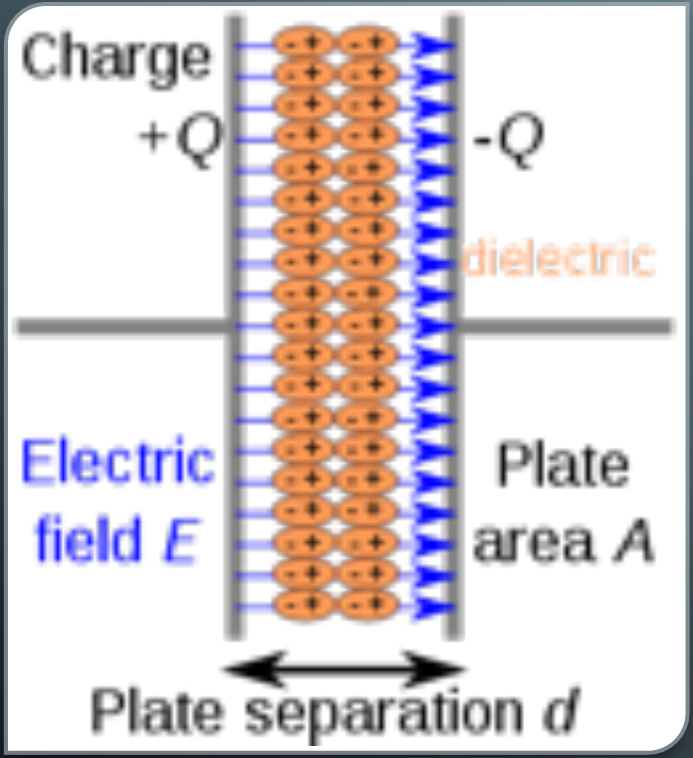
# SUPERCAPACITORS: ELECTRODE AND ELECTROLYTE MATERIALS

ROHMA KHAN

# SUPERCAPACITOR REVIEW

DESIGN, BENEFITS

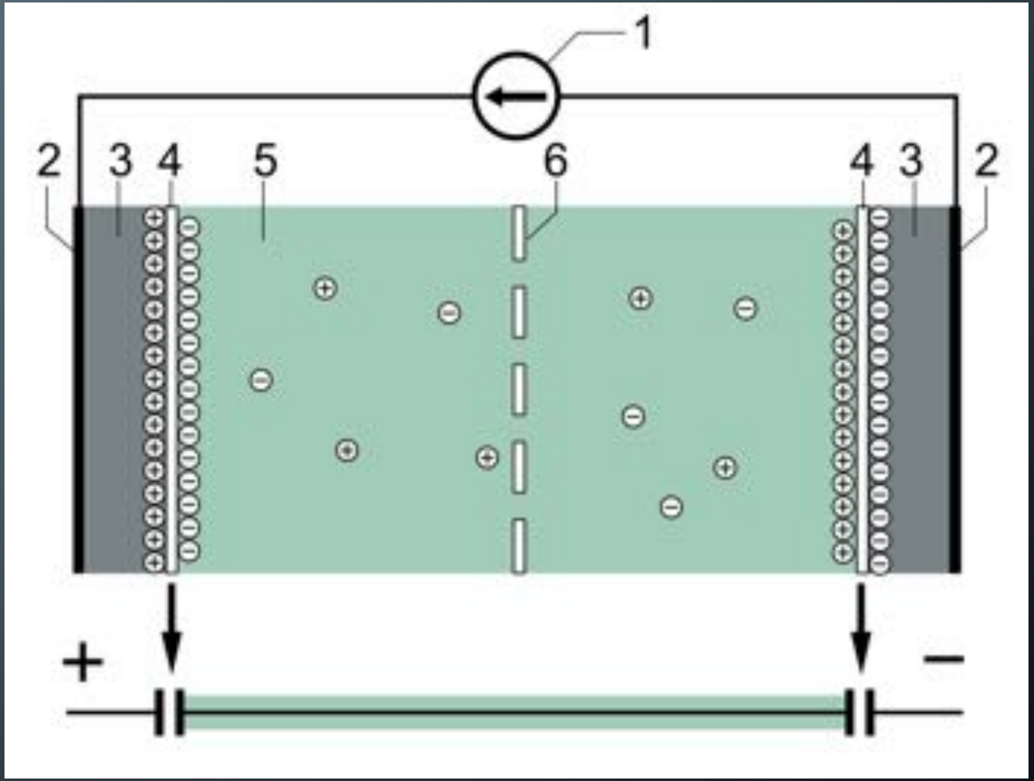
# WHAT IS A CAPACITOR? [1]



- A capacitor is an energy storage device consisting of two parallel conducting plates separated by some insulating dielectric material. When a voltage is applied across a capacitor, it develops an electric field, polarizing the dielectric material, and thus storing charge.
- Energy Stored in a Capacitor is: $U = \frac{1}{2}CV^2$
  - Higher Capacitance means higher energy stored!
- Max Power of a Capacitor is: $P_{max} = \frac{V^2}{4*ESR}$
- In order to increase Energy stored in a capacitor we have to increase Capacitance!
- Capacitance: $C = \frac{Q}{V} = \varepsilon_r \varepsilon_0 \frac{A}{d}$ (measured in Farads)
- How to increase Capacitance? Increase plate area A, or increase $\varepsilon_r$.

# SUPERCAPACITORS

- Supercapacitors, also known as ultracapacitors or EDLCs, are essentially “high capacity capacitors”.
- The electric double-layer capacitors (EDLCs) are composed of two carbon-based electrodes, an electrolyte and a separator. Ions in the electrolyte accumulate on the electrode and form an electric double layer of opposite polarity.



(1) power source, (2) collector, (3) polarized electrode, (4) Helmholtz double layer, (5) electrolyte having positive and negative ions, (6) separator

## BENEFITS

- High Power Output
- Fast Charge and Discharge
- Low Internal Resistance
- No Chemical Reactions = Long Life Cycle
- Long life cycle
- Low internal resistance

## DISADVANTAGES

- Low Energy Density
- High Self-Discharge
- Low Maximum Voltage
- Rapid Voltage Drop

# WHAT ARE WE TESTING FOR?

- “Three technical characteristics often dictate which particular energy storage technology is selected for a given application: 1) energy/volume, which ultimately establishes the physical size of the storage system; 2) charge time/discharge time, which must be compatible with the intended use; and 3) cycle life, which often dictates the operational life of an energy storage system. In some applications, non-technical characteristics like cost and safety have importance equal to the technical characteristics.” [2]

# TWO TYPES OF TESTS

- Cyclic Voltammetry (CV) helps us test for Cycle Life, Capacitance and Voltage Window. Like its name suggests Cyclic Voltammetry is done by applying voltage sweep to the circuit and measuring the current. We can measure the capacitance of the supercapacitor by measuring the current and then solving for $I=C\ dV/dt$. [3]
- Energy Density, Power Density and charge/discharge time can be found using Galvanostatic Cycling Tests. Galvanostatic cycling consist of varying current and measuring the potential. [4]

# WHAT CAN WE REPLACE IONIC LIQUIDS WITH THAT WOULD WORK THE SAME OR BETTER? CAN WE USE DEEP EUTECTIC SOLVENTS TO REPLACE IONIC LIQUIDS?

RESEARCH QUESTIONS

# ELECTROLYTES

- The electrolyte chosen for our supercapacitor determines a lot of its characteristics. An ideal electrolyte has high electrochemical/ thermal/ chemical stability, low melting point, high boiling point, and be cheap. There are three main types used ionic liquids, aqueous electrolytes or organic electrolytes.
- Ionic liquids are most typically used with EDLCs. Ionic liquids are liquid salts that do not contain neutral solvent molecules. [5]

# LITERATURE SEARCH ON USE OF IONIC LIQUIDS IN SUPERCAPACITORS

# IONIC LIQUIDS FOR SUPERCAPACITOR APPLICATIONS MATHIEU SALANNE [5]

- Found that Ionic Liquids have an electrical conductivity and diffusion coefficient much smaller than that of organic electrolytes.
- Ionic Liquids are stable at high temperatures, with a high boiling point. However they, in general, have melting points at room temperatures. This prevents them from being used in current commercial applications. Found that this could be overcome by mixing two ionic liquids that share an anion but have different cations.
- Despite having a higher voltage window, and boiling temp due to their other factors ILs best case may be mixing them with organic solvents.

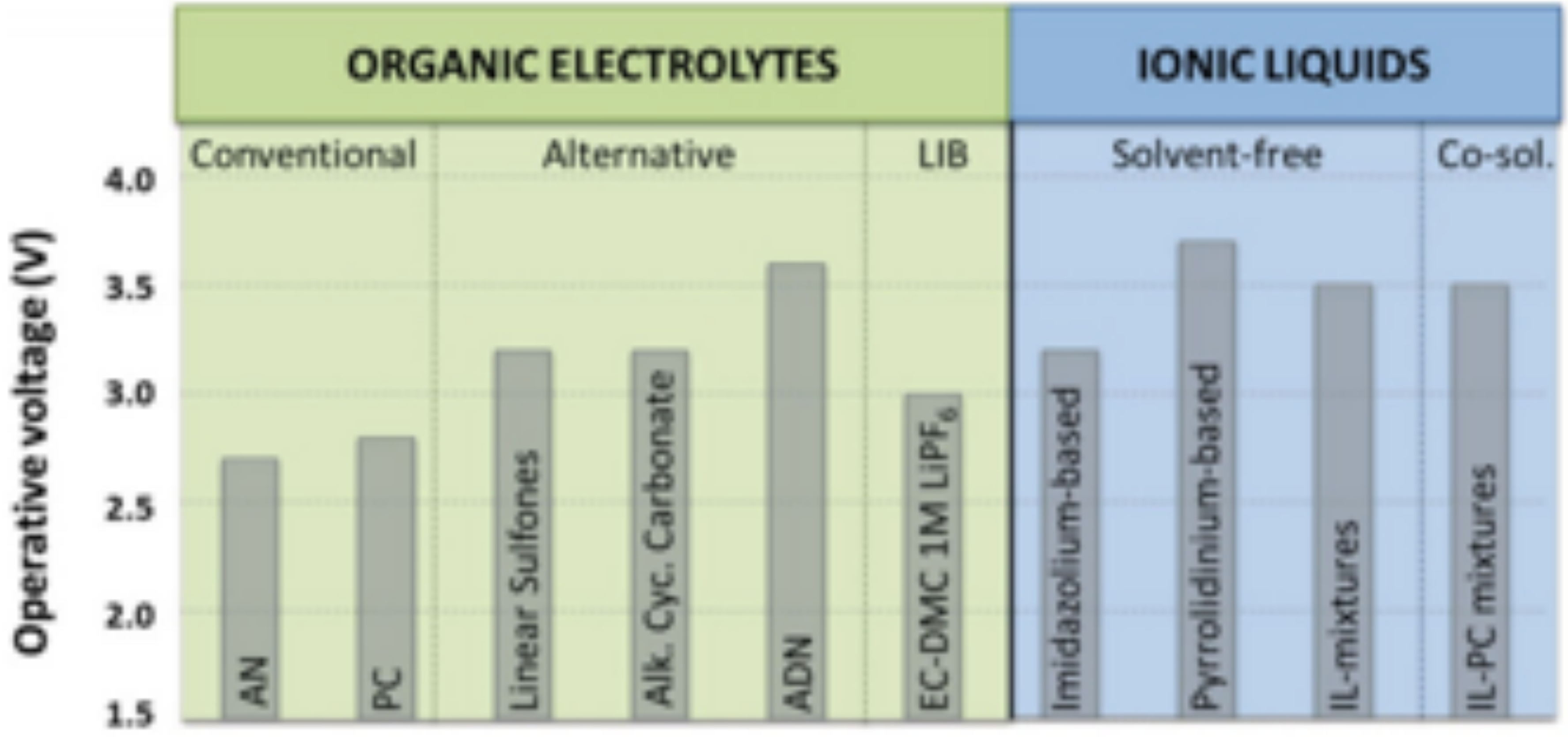


**Fig. 3** Comparison of the EDLCs operating voltage achievable with organic electrolyte and ionic liquids based electrolytes. *AN* acetonitrile, *PC* propylene carbonate, *ADN* adiponitrile, *Alkylat. Cyc. Carb.* alkylated cyclic carbonate, *EC* ethylene carbonate, *DMC* dimethyl carbonate, *LiPF* $_6$ lithium hexafluorophosphate, *IL* ionic liquids. Reproduced with permission from Ref. [4]

# SUPERCAPACITORS UTILISING IONIC LIQUIDS ALI EFTEKHARIAB [6]

- Reviewed the role of different Ionic Liquids in Supercapacitor designs. Found that ILs have a wider more stable potential window than usual organic electrolytes. We should look at ILs as a source for ions not as the main electrolyte. This is because ILs have a high viscosity and are expensive, making them difficult to commercially develop.
- Found mixing ILs in gel polymer electrolytes improves thermal stability and increases the stable electrochemical window.
- Mixing ILs may yield the best results. Introducing different ions within the Ionic Liquid can improve capacitive performance.

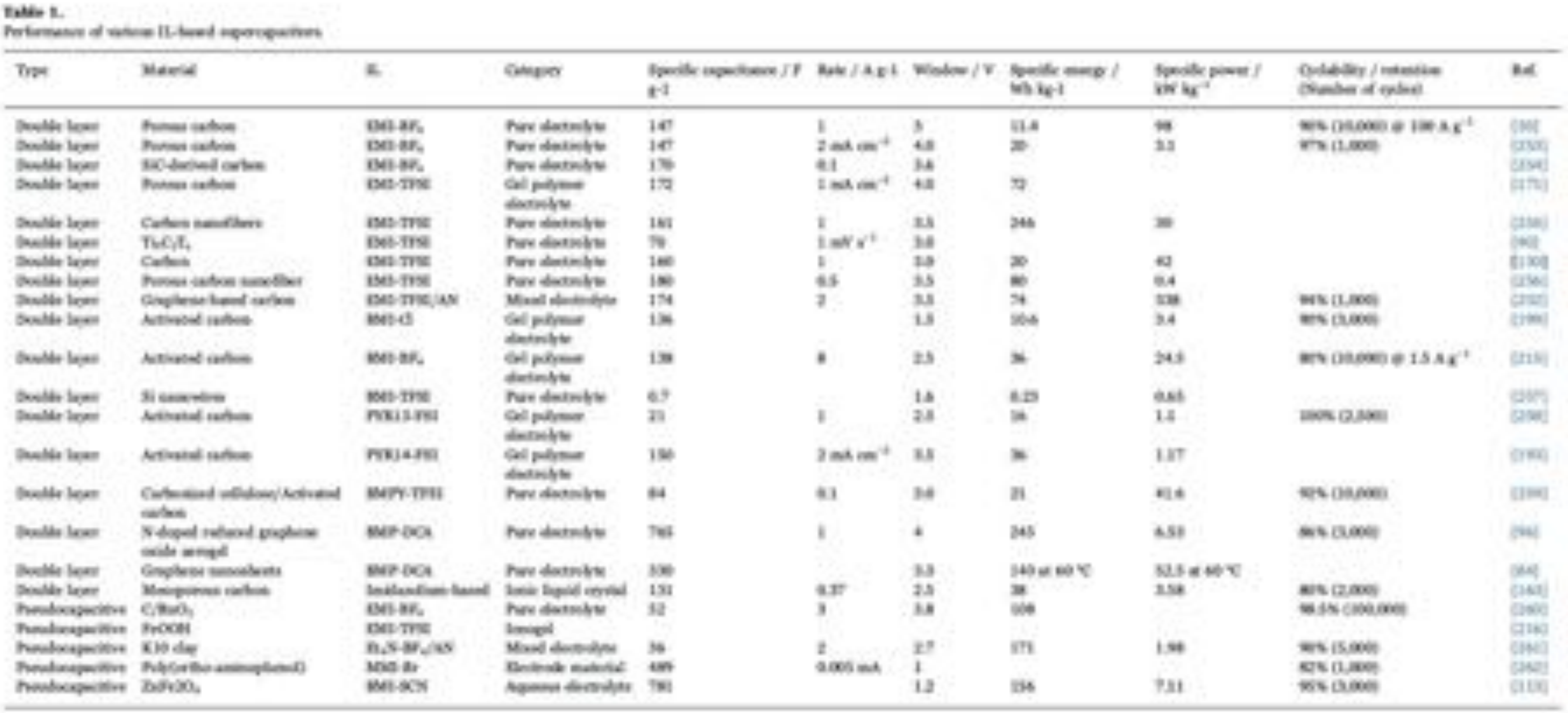


**Table 1.**

Performance of various IL-based supercapacitors.

| Type | Material | IL | Category | Specific capacitance / F g-1 | Rate / A g-1 | Window / V | Specific energy / Wh kg-1 | Specific power / kW $kg^{-1}$ | Cyclability / retention (Number of cycles) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Double layer | Porous carbon | EMI-$BF_4$ | Pure electrolyte | 147 | 1 | 3 | 11.4 | 98 | 90% (10,000) @ 100 A $g^{-1}$ | [30] |
| Double layer | Porous carbon | EMI-$BF_4$ | Pure electrolyte | 147 | 2 mA $cm^{-2}$ | 4.0 | 20 | 3.1 | 97% (1,000) | [253] |
| Double layer | SiC-derived carbon | EMI-$BF_4$ | Pure electrolyte | 170 | 0.1 | 3.6 | | | | [254] |
| Double layer | Porous carbon | EMI-TFSI | Gel polymer electrolyte | 172 | 1 mA $cm^{-2}$ | 4.0 | 72 | | | [175] |
| Double layer | Carbon nanofibers | EMI-TFSI | Pure electrolyte | 161 | 1 | 3.5 | 246 | 30 | | [255] |
| Double layer | $Ti_3C_2T_x$ | EMI-TFSI | Pure electrolyte | 70 | 1 mV $s^{-1}$ | 3.0 | | | | [90] |
| Double layer | Carbon | EMI-TFSI | Pure electrolyte | 160 | 1 | 3.0 | 20 | 42 | | [130] |
| Double layer | Porous carbon nanofiber | EMI-TFSI | Pure electrolyte | 180 | 0.5 | 3.5 | 80 | 0.4 | | [256] |
| Double layer | Graphene-based carbon | EMI-TFSI/AN | Mixed electrolyte | 174 | 2 | 3.5 | 74 | 338 | 94% (1,000) | [252] |
| Double layer | Activated carbon | BMI-Cl | Gel polymer electrolyte | 136 | | 1.5 | 10.6 | 3.4 | 90% (3,000) | [199] |
| Double layer | Activated carbon | BMI-$BF_4$ | Gel polymer electrolyte | 138 | 8 | 2.5 | 36 | 24.5 | 80% (10,000) @ 1.5 A $g^{-1}$ | [215] |
| Double layer | Si nanowires | BMI-TFSI | Pure electrolyte | 0.7 | | 1.6 | 0.23 | 0.65 | | [257] |
| Double layer | Activated carbon | PYR13-FSI | Gel polymer electrolyte | 21 | 1 | 2.0 | 16 | 1.2 | 100% (2,500) | [258] |
| Double layer | Activated carbon | PYR14-FSI | Gel polymer electrolyte | 150 | 2 mA $cm^{-2}$ | 3.5 | 36 | 1.17 | | [195] |
| Double layer | Carbonized cellulose/Activated carbon | BMPY-TFSI | Pure electrolyte | 84 | 0.1 | 3.0 | 21 | 41.6 | 92% (10,000) | [159] |
| Double layer | N-doped reduced graphene oxide aerogel | BMP-DCA | Pure electrolyte | 765 | 1 | 4 | 245 | 6.53 | 86% (3,000) | [96] |
| Double layer | Graphene nanosheets | BMP-DCA | Pure electrolyte | 330 | | 3.3 | 140 at 60 °C | 52.5 at 60 °C | | [64] |
| Double layer | Mesoporous carbon | Imidazolium-based | Ionic liquid crystal | 131 | 0.37 | 2.5 | 38 | 3.58 | 80% (2,000) | [163] |
| Pseudocapacitive | $C/RuO_2$ | EMI-$BF_4$ | Pure electrolyte | 32 | 3 | 3.8 | 108 | | 98.5% (100,000) | [260] |
| Pseudocapacitive | FeOOH | EMI-TFSI | Ionogel | | | | | | | [216] |
| Pseudocapacitive | K10 clay | $Et_4N$-$BF_4$/AN | Mixed electrolyte | 36 | 2 | 2.7 | 171 | 1.98 | 90% (5,000) | [261] |
| Pseudocapacitive | Poly(ortho-aminophenol) | MMI-Br | Electrode material | 489 | 0.005 mA | 1 | | | 82% (1,000) | [262] |
| Pseudocapacitive | $ZnFe2O_4$ | BMI-SCN | Aqueous electrolyte | 781 | | 1.2 | 156 | 7.11 | 95% (3,000) | [113] |

This table shows electrolytes effects on supercapacitor characteristics. [6]

# DEEP EUTECTIC SOLVENTS

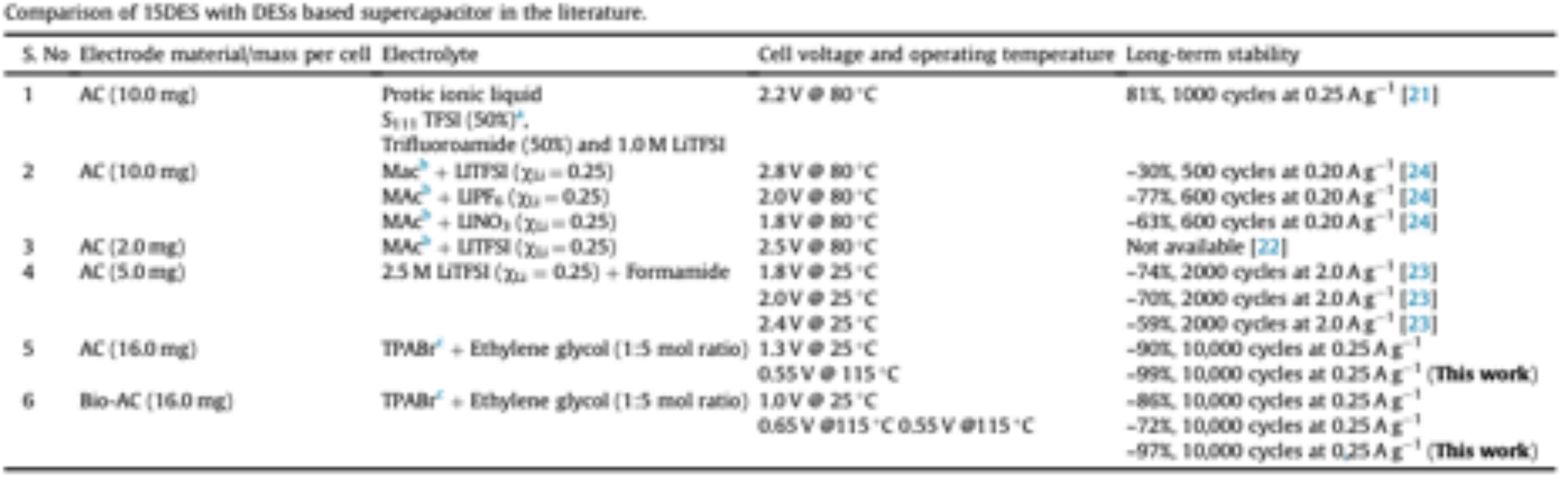
- Deep Eutectic Solvents are ionic liquid analogues, containing nonsymmetric ions. They are liquids that are eutectic mixtures of salts and hydrogen bond donors (whose combination gives a melting point lower than the individual components do). [7]
- Both previous studies mention using Deep Eutectic Solvents as possible electrolytes. Note: Deep eutectic solvents have been used to create electrodes in most of the articles I found.
- DES are attractive because they have a low-cost, easy preparations, bio-compatible, bio-degradable and non-toxic nature. [8]

# LITERATURE SEARCH ON USE OF DEEP EUTECTIC SOLVENTS AS ELECTROLYTES IN SUPERCAPACITORS

# ENVIRONMENTALLY BENIGN NON-FLUORO DEEP EUTECTIC SOLVENT AND FREESTANDING RICE HUSK-DERIVED BIO-CARBON BASED HIGH-TEMPERATURE SUPERCAPACITORS

## SETHURAMAN SATHYAMOORTHI, NUTTHAPHON PHATTHARASUPAKUN, MONTREE SAWANGPHRUK [8]

- Tested an ethylene glycol and tetrapropylammonium bromide based non-fluoro DESs as electrolytes for the supercapacitor. This was the first time it was tested as electrolytes for supercapacitors. For the electrode they used free-standing microporous commercial activated carbon (AC) and mesoporous rice husk-derived bio-activated carbon (Bio-AC) were used.
- Results: The DES can be operational at temperatures as high as 115 °C. The ratio of 1: 5 of TEABr and EG had the lowest viscosity and highest compared to other two compositions.



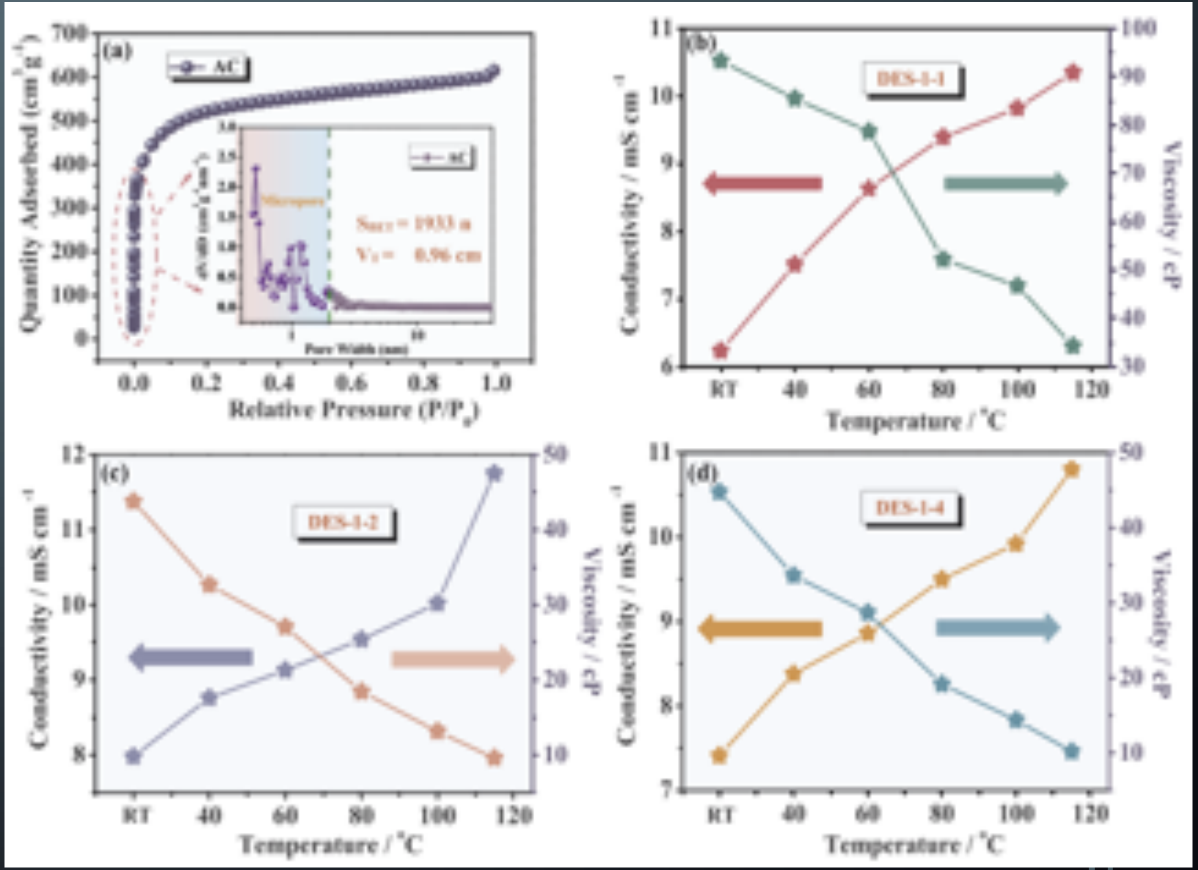
Comparison of 15DES with DESs based supercapacitor in the literature.

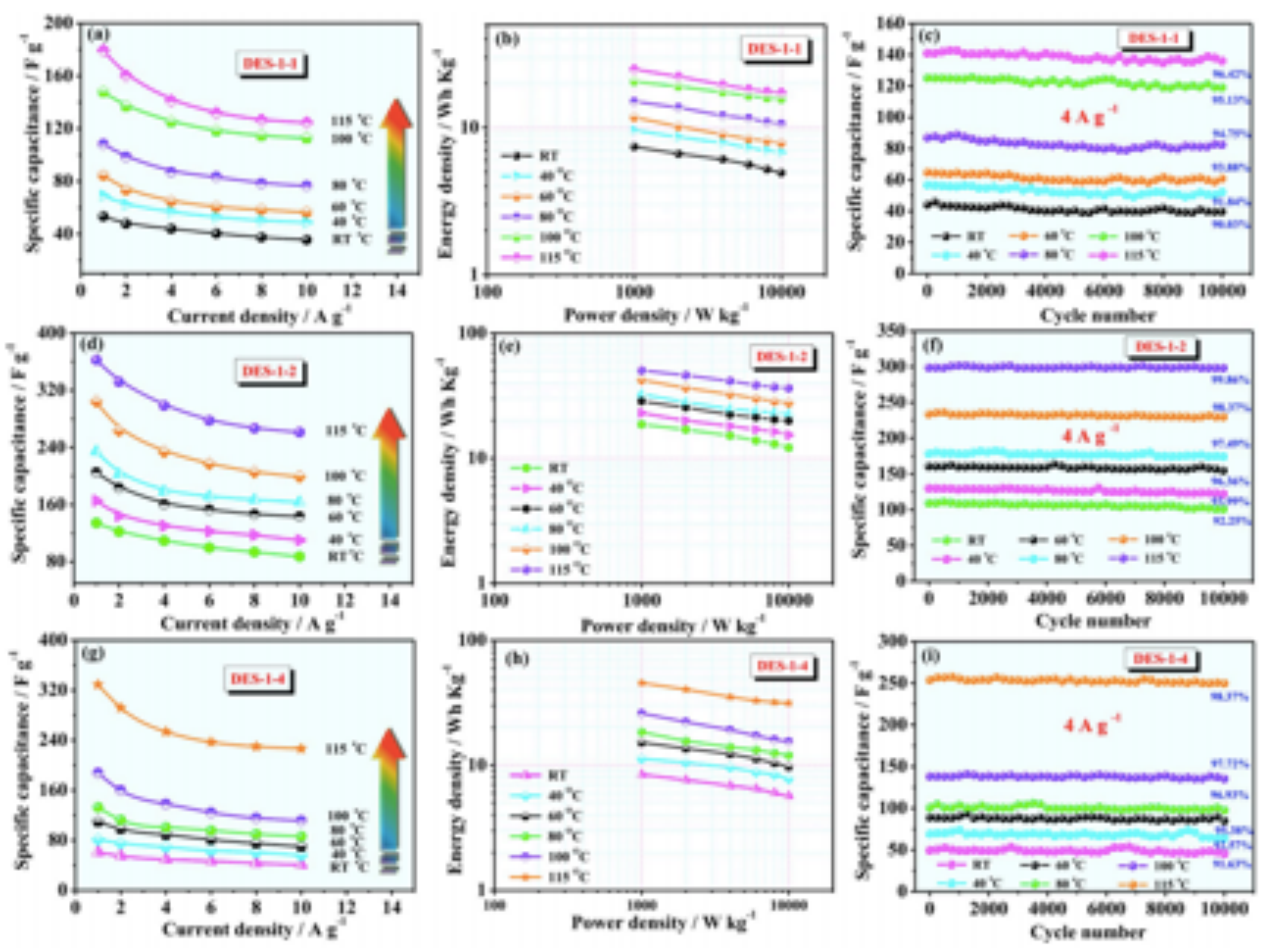
| S. No | Electrode material/mass per cell | Electrolyte | Cell voltage and operating temperature | Long-term stability |
|---|---|---|---|---|
| 1 | AC (10.0 mg) | Protic ionic liquid<br>$S_{111}$ TFSI (50%)[a],<br>Trifluoroamide (50%) and 1.0 M LiTFSI | 2.2 V @ 80 °C | 81%, 1000 cycles at 0.25 A $g^{-1}$ [21] |
| 2 | AC (10.0 mg) | Mac[b] + LiTFSI ($\chi_{Li} = 0.25$) | 2.8 V @ 80 °C | ~30%, 500 cycles at 0.20 A $g^{-1}$ [24] |
|  |  | MAc[b] + $LiPF_6$ ($\chi_{Li} = 0.25$) | 2.0 V @ 80 °C | ~77%, 600 cycles at 0.20 A $g^{-1}$ [24] |
|  |  | MAc[b] + $LiNO_3$ ($\chi_{Li} = 0.25$) | 1.8 V @ 80 °C | ~63%, 600 cycles at 0.20 A $g^{-1}$ [24] |
| 3 | AC (2.0 mg) | MAc[b] + LiTFSI ($\chi_{Li} = 0.25$) | 2.5 V @ 80 °C | Not available [22] |
| 4 | AC (5.0 mg) | 2.5 M LiTFSI ($\chi_{Li} = 0.25$) + Formamide | 1.8 V @ 25 °C | ~74%, 2000 cycles at 2.0 A $g^{-1}$ [23] |
|  |  |  | 2.0 V @ 25 °C | ~70%, 2000 cycles at 2.0 A $g^{-1}$ [23] |
|  |  |  | 2.4 V @ 25 °C | ~59%, 2000 cycles at 2.0 A $g^{-1}$ [23] |
| 5 | AC (16.0 mg) | TPABr[c] + Ethylene glycol (1:5 mol ratio) | 1.3 V @ 25 °C | ~90%, 10,000 cycles at 0.25 A $g^{-1}$ |
|  |  |  | 0.55 V @ 115 °C | ~99%, 10,000 cycles at 0.25 A $g^{-1}$ (**This work**) |
| 6 | Bio-AC (16.0 mg) | TPABr[c] + Ethylene glycol (1:5 mol ratio) | 1.0 V @ 25 °C | ~86%, 10,000 cycles at 0.25 A $g^{-1}$ |
|  |  |  | 0.65 V @115 °C 0.55 V @115 °C | ~72%, 10,000 cycles at 0.25 A $g^{-1}$ |
|  |  |  |  | ~97%, 10,000 cycles at 0.25 A $g^{-1}$ (**This work**) |

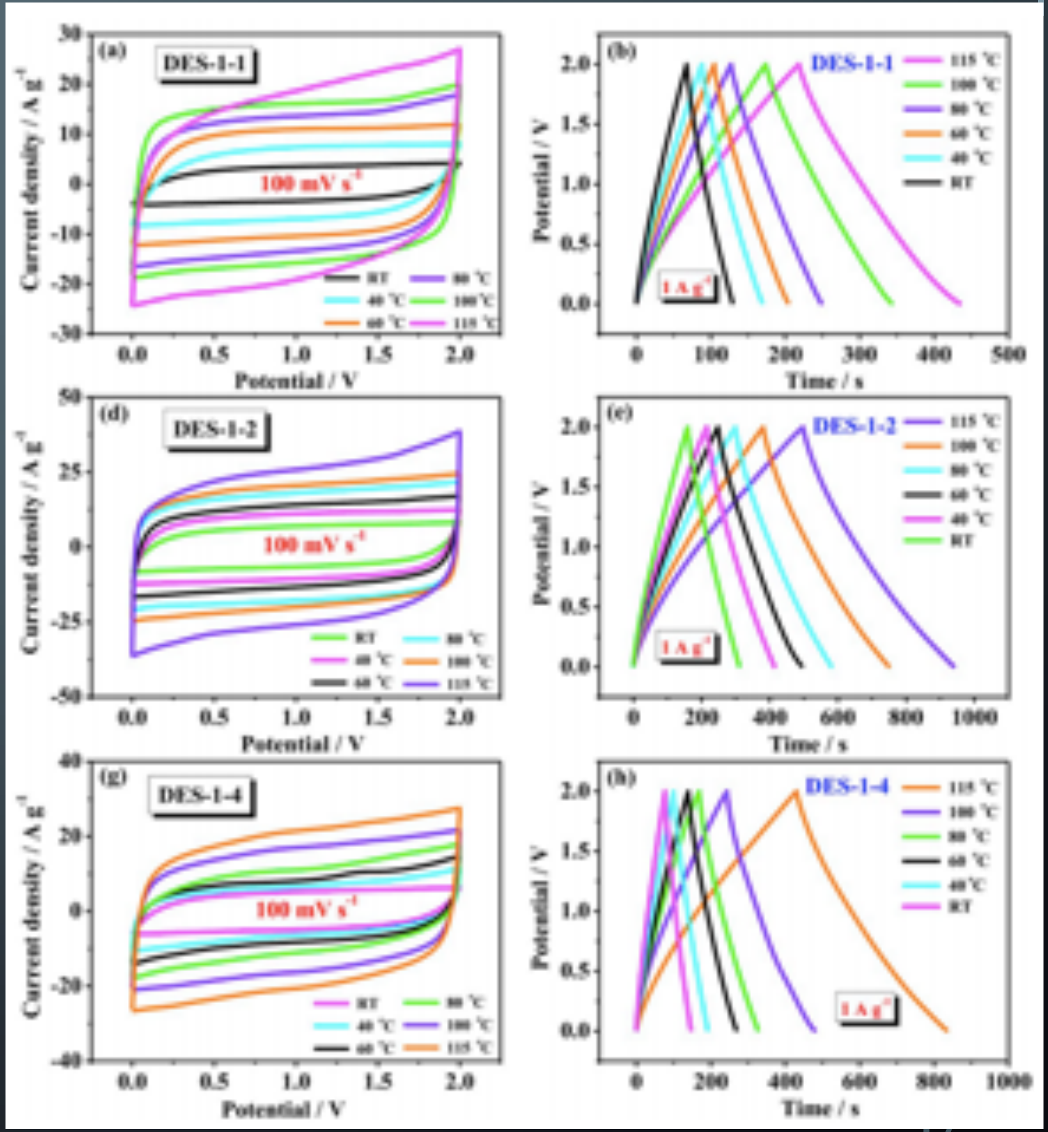
- Concluded supercapacitors may be used at high temperatures.

# AN ALTERNATIVE ELECTROLYTE OF DEEP EUTECTIC SOLVENT BY CHOLINE CHLORIDE AND ETHYLENE GLYCOL FOR WIDE TEMPERATURE RANGE SUPERCAPACITORS [9]

- Compared DES with different molar ratios of ChCl and EG. Found that the DES has low viscosity, high electrical conductivity, and as temperature increases viscosity goes down while conductivity goes up.
- Result: DES-1-2 has higher specific capacitance, energy density and cyclic stability at the same temperature.




(a)
DES-1-1
Specific capacitance / F g⁻¹
Current density / A g⁻¹
115 °C
100 °C
80 °C
60 °C
40 °C
RT °C
(b)
DES-1-1
Energy density / Wh Kg⁻¹
Power density / W kg⁻¹
RT
40 °C
60 °C
80 °C
100 °C
115 °C
(c)
DES-1-1
4 A g⁻¹
Specific capacitance / F g⁻¹
Cycle number
(d)
DES-1-2
Specific capacitance / F g⁻¹
Current density / A g⁻¹
(e)
DES-1-2
Energy density / Wh Kg⁻¹
Power density / W kg⁻¹
(f)
DES-1-2
4 A g⁻¹
Specific capacitance / F g⁻¹
Cycle number
(g)
DES-1-4
Specific capacitance / F g⁻¹
Current density / A g⁻¹
(h)
DES-1-4
Energy density / Wh kg⁻¹
Power density / W kg⁻¹
(i)
DES-1-4
4 A g⁻¹
Specific capacitance / F g⁻¹
Cycle number


(a)
DES-1-1
100 mV s⁻¹
Current density / A g⁻¹
Potential / V
RT
40 °C
60 °C
80 °C
100 °C
115 °C
(b)
DES-1-1
1 A g⁻¹
Potential / V
Time / s
(d)
DES-1-2
100 mV s⁻¹
Current density / A g⁻¹
Potential / V
(e)
DES-1-2
1 A g⁻¹
Potential / V
Time / s
(g)
DES-1-4
100 mV s⁻¹
Current density / A g⁻¹
Potential / V
(h)
DES-1-4
1 A g⁻¹
Potential / V
Time / s

# ALL-CLIMATE AQUEOUS SUPERCAPACITOR ENABLED BY A DEEP EUTECTIC SOLVENT ELECTROLYTE BASED ON SALT HYDRATE [10]

- Inspired by wanting to keep the benefits of aqueous electrolytes at low temperatures. Used mixture of Mg(ClO4)2·6H2O and water at the eutectic concentration as electrolyte. Used activated carbon electrode. Compared the 3.5 m Mg(ClO4)2 DES to 1.0 m Na2SO4 and the hypoeutectic Mg(ClO4)2 (1.0 m) solution.
- Results found the 3.5 m Mg(ClO4)2 DES to be cheap to make, good at extreme temperatures and have a very good cycle life.

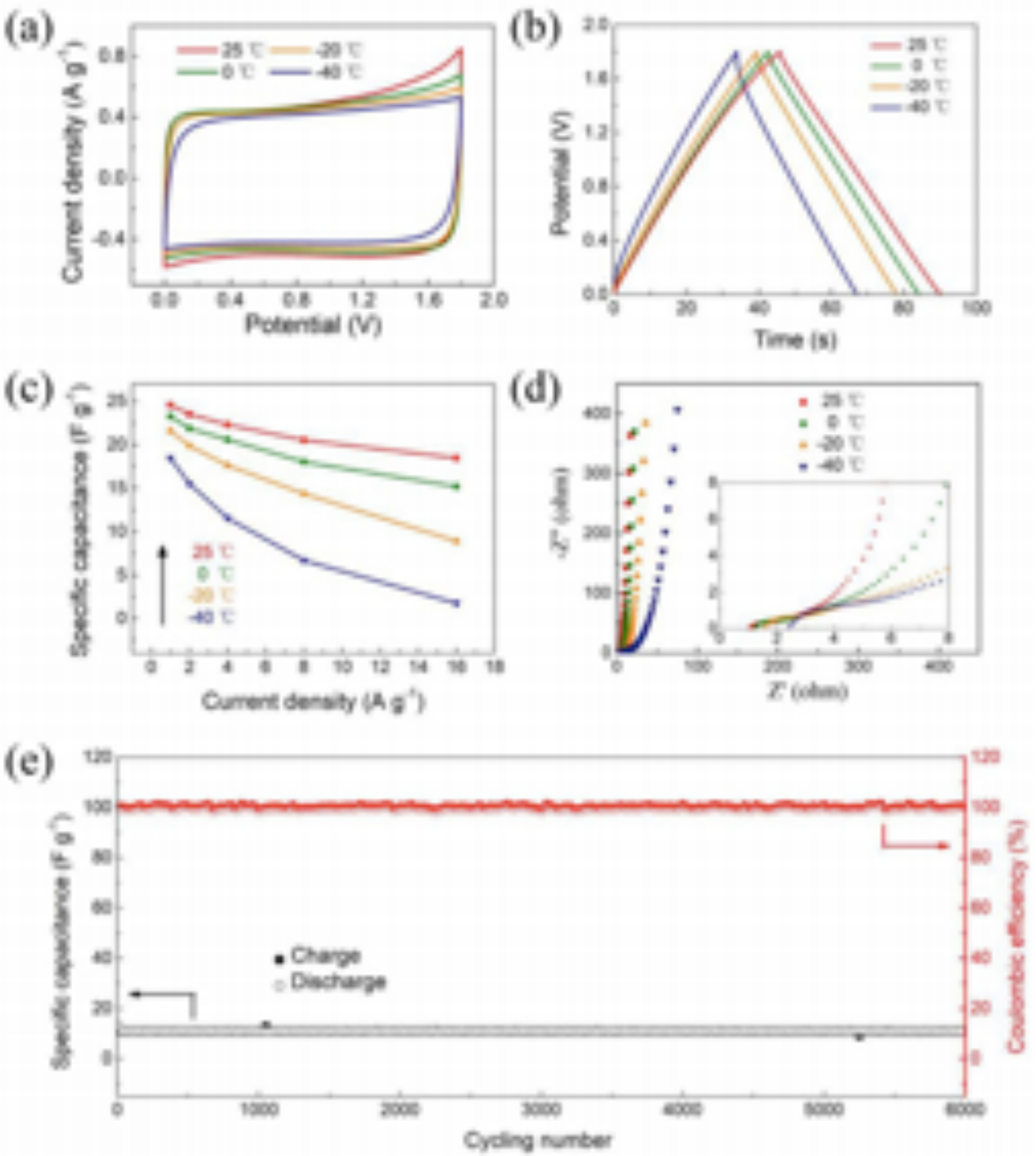


**Fig. 6.** Comparison of the electrochemical performance of the 1.8 V SC with 3.5 m $Mg(ClO_4)_2$ electrolyte at temperature of 25, 0, −20, −40 °C. (a) CV curves at a scan rate of 20 mV $s^{-1}$. (b) GCD curves at a current density of 1 A $g^{-1}$. (c) Specific capacitance at different current densities. (d) Nyquist plots and (inset) the data in high-frequency ranges. (e) The cyclic stability and Coulombic efficiency of −40 °C at a current density of 4 A $g^{-1}$.

# CONCLUSION

- Deep eutectic solvents are not highly tested or used as electrolytes in supercapacitors, but have the potential to be so.
- Right now the DES electrolyte is still in development, but due to its wide temperature range, budget-friendliness and easy prep focus has began to be placed on it.

# USES FOR SUPERCAPACITORS

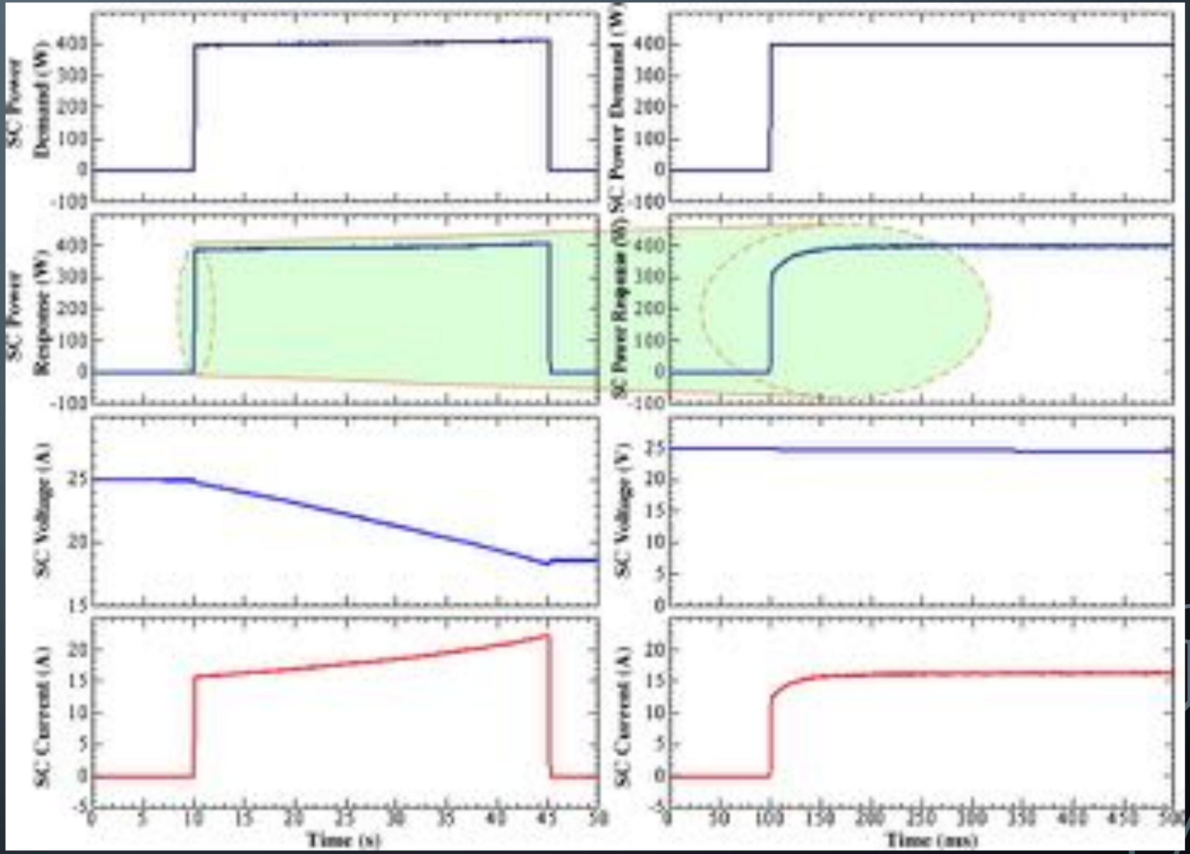
## WHY DOES THIS MATTER?

- “Used mobile phones, laptop computers, heavy duty vehicles, motor racing, UPS and in aircrafts.
- Ultracapacitor Functions
- Secure power
- Provides reliable interim power, even if the primary source fails or fluctuates
- Energy storage
- Stores energy from low power sources, enabling support for high power loads
- Pulse power
- Supplies peak power to the load while drawing average power from the source
- Reduces the size & weight of the battery / power source required
- Improves run-time & battery life, particularly at cold temperatures
- Enables more power-hungry features, being used more often
- Can remove the need for a battery & harvest energy from clean sources
- Protects against accidental power loss or fluctuations/interruptions
- Doesn’t need to be replaced like batteries (unlimited discharge cycles)
- Environmentally friendly & safe”

[11]

# ENERGY MANAGEMENT OF FUEL CELL/SOLAR CELL/SUPERCAPACITOR HYBRID POWER SOURCE

- They were able to build a working hybrid energy system with a renewable energy source. The Supercapacitor was an energy storage device because of its’ fast power response and high specific power.



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