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Modifying potato starch by glutaraldehyde and $MgCl_2$ for developing an economical and environment-friendly electrolyte system

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Abstract: Biodegradable polymer electrolyte systems are the most sought over option for cheap and energy efficient storage devices. Present paper discusses the results of potato starch + $MgCl_2$ system which satisfy the technical and economic criteria to become a potential candidate for future electrolyte systems. The developed system has high ionic conductivity (~3.43×10^{-2} S/cm), low relaxation time (75 μs) and wide electrochemical stability window (ESW ~4.6 V). The phase angle approaches -79° and maintains its value for 10 Hz to 1 kHz frequency range. The prepared material is a free standing film which can be bended and twisted up to 90°, which makes it suitable for flexible electrochemical device fabrication. The equivalent series resistance (ESR) is quite low (3.41 Ω) and self-resonance frequency below which energy can be efficiently stored is approximately 0.1 MHz. Hence the present study reports an economical, easy to handle and environment friendly electrolyte suitable for electrochemical device fabrication.

Keywords: biopolymer; flexible electrolyte; ESR; ESW; short ion relaxation time

1 Introduction

Urbanization has paved the way for higher levels of comfort and standard of living. Rapid urbanization and faster growth of economy has led to an enormous increase in energy needs. Conventional sources of energy are no longer an option to be sought over since they are destined to deplete in near future and cause global warming. Considering the need of future generation and planning the utilization of our environment and resources wisely, researchers are looking for renewable energy sources (1-3). Unfortunately poor energy efficiency and reliability on weather conditions puts a big hurdle on their exploitation to full capacity, thus requiring small-scale energy storage devices such as batteries, supercapacitors and fuel cells (4-7). Supercapacitors have energy densities greater than those of conventional capacitors and power densities greater than those of batteries. As a result, supercapacitors have emerged as an attractive option for an increasing number of applications. These devices are parameterised by the properties such as high capacitance, low equivalent series resistance (ESR) value, high power density, better thermal stability, and fast charging – discharging rate. Several devices are being proposed for understanding the proper characteristics of electrode, electrolyte and their congruency. Capacity, being more obvious parameter for supercapacitors, has attracted the scientific community to find better electrodes as it is the capacity deciding factor (8-12). For practical applicability, capacity is not the only technical required parameter. It should have good energy density and power density which is decided by electrolytes. Hence in recent past studies targeting better electrolyte systems could also be seen in literature. The aqueous and non-aqueous liquid electrolytes are generally used to study new electrode material but they have low electrochemical stability window (ESW) and resulting in low energy and power density because these parameters depends upon square of ESW. Ionic liquids have better ESW (~4 V) but they are not cost effective material for commercial applications. Hydrogel and polymer electrolytes are also tried for supercapacitor fabrication where observed ESW is of the order of ~2.5 V. Polymer electrolytes having favourable properties for designing and stability of devices have received greater scientific attention.

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Armand and co-workers (13-15) introduced polymer electrolytes to electrochemists, since then worldwide scientists are working in the field to improve the polymer electrolytes (16,17). The viscoelastic nature of polymers, which combines both liquid and solid like behaviour, makes it a perfect choice for all electrochemical applications. Natural polymer electrolytes being renewable, eco-friendly, economical, naturally abundant and having tremendous tailoring properties have come out as researchers most sought over choice in past few decades. Chitosan, agar-agar, starch, cellulose, pectin etc. (18-31) have been used as natural host for electrolyte preparation. The aqueous and non-aqueous mediums have been used for the electrolyte preparation but, since aqueous medium based membranes faces retrogradation and they are more prone to attack of microorganism and hence non-aqueous solvents are preferred (32,33). A summary of electrolytes and their electrochemical parameters are summarized in Table 1. Although many of the electrolytes seem to have conductivity >10^{-4} S/cm and reported to be used in devices also but it has to be noted that either the ESR value is not reported or it is very high. Another important factor is that except few, all of them have some amount of additive which is to enhance the conductivity. Literature survey indicated that starch, a natural polymer available in variety and ready to accept salt in good quantity, presents itself as potential candidate for electrolyte preparation. However, it also gets easily infected from fungus as it is a direct food for living organisms. Our group resolved this problem using glutaraldehyde (GA) as a crosslinker and/or preservative (34). Several starches like corn, arrowroot, wheat and rice have been studied in different orientations (35,36). Present paper deals with the properties of potato starch + $MgCl_2$ + GA system.

Morphologically, potato starch is found to be better than other starches (37). Li is supposed to be the best salt for synthesis of polymer-salt complex electrolytes but it has many drawbacks and its natural sources are limited. Hence alternate salts having comparable electrochemical properties are being sought and it has been established that sodium and magnesium salts are the prospective alternates. Sodium salt based potato starch electrolytes have already been established as potential candidate for electrochemical device fabrications (38). In present study magnesium chloride based system is studied.

2 Experimental

2.1 Material preparation

Potato starch $(C_6H_{10}O_5)_n$ received from Molychem, India, magnesium chloride ($MgCl_2$) and glutaraldehyde (GA) ($C_5H_8O_2$), purchased from Merck, India, and methanol (CH_3OH) from Fischer Scientific, India, have been used to prepare the sample. Simple and cost-effective solution cast technique was used for material preparation. A series of samples with different $MgCl_2$ concentrations (0.4 to 2 g) for fixed starch concentration (1 g) has been prepared. One gram of potato starch in 20 mL of methanol has been stirred, followed by adding $MgCl_2$ solution in methanol

Table 1: Comparing different electrochemical parameters of natural polymer based electrolytes.

Polymer+Salt	ESR (Ω)	Conductivity (S/cm)	Relaxation time (µs)	Ea (eV)	ESW (V)	Ref
Agar-agar (50%) + NH_4Br (50%) + EC(0.3%)	.....	3.73×10^{-4}	2µs	.....	.....	(18)
Agar (40%) + NH_4NO_3 (60%) + 40 wt% glycerol	.....	1.44×10^{-3}	.....	.....	.....	(19)
Agar-agar (50 wt%) + NH_4I (50 wt%)	.....	1.2×10^{-4}	.....	0.43	2.4	(20)
Agar-agar (50 wt%) + NH_4Br (50 wt%)	.....	1.33×10^{-4}	.....	0.24	2.5	(20)
Bacto agar + NaI (1.6 M) + 50 µL I_2		1.04×10^{-3}	.....	.....	1.8	(21)
Sodium Carboxy methyl **cellulose +** PEO + $NaClO_4$	65000	$\sim 10^{-6}$	.....	.....	4.5	(22)
Cellulose + Ionic liquid + KOH	.....	3.25×10^{-1}	.....	.....	.....	(23)
Hydroxyethyl **cellulose** (HEC) + $LiPF_6$ + EC/DMC/EMC (1:1:1)	.....	1.8×10^{-4}	.....	0.04	5	(24)
Chitosan + starch (60:40)	1500	3.7×10^{-4}	.....	.....	.....	(25)
chitosan + Mg $(Tf)_2$/EMITf	.....	3.57×10^{-5}	1.3	0.72	4.2	(26)
Chitosan + IL + acetic acid + LiCl	.....	3.23×10^{-3}	.....	0.14	4.0	(27)
Chitosan + IL + adipic acid + LiCl	.....	4.66×10^{-3}	.....	0.22	.....	(27)
Gelatin + acetic acid (26.3 wt%) + glycerol	.....	4.5×10^{-5}	.....	0.33	.....	(28)
Pectin + NH_4NO_3 (70:30)	.....	6.68×10^{-5}	.....	0.11	.....	(29)
Pectin + IL + Glycerol	.....	1.43×10^{-6}	.....	.....	.....	(30)
Pectin + Glycerol (68%) + $LiClO_4$	.....	4.7×10^{-4}	.....	.....	3.0	(31)

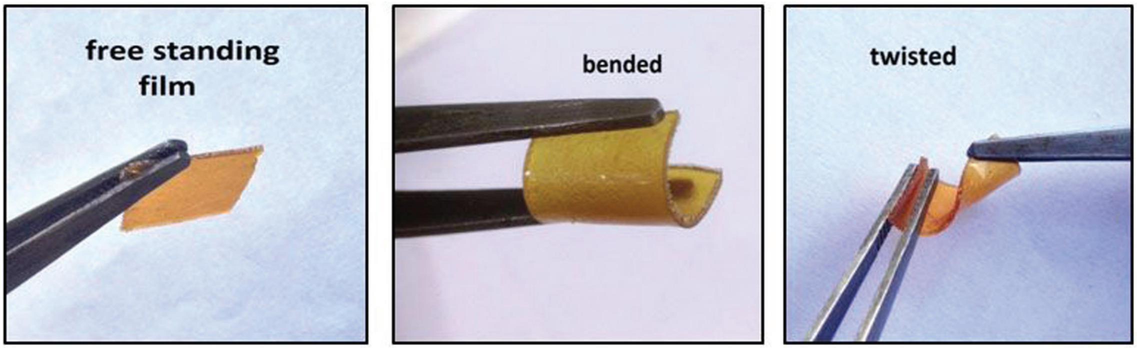

Figure 1: Pictorial representation of synthesized material's bending and twisting ability.

to the mixture at 40°C. 2 mL of GA has been added after few minutes to the stirring mixture in order to obtain a homogeneous solution. The mixture was then poured in a petri dish and left for drying at ambient conditions. A free standing film is obtained after almost a week. Prepared material's texture changes from hard to soft with increasing salt concentration. The prepared materials are very flexible and can be twisted easily as shown in Figure 1.

2.2 Characterization techniques

The prepared samples were cut into square pieces of 10 × 10 mm^2 using a sharp scissor. Aluminium foils were used as electrode for the electrochemical impedance spectroscopy (EIS) measurements. EIS measurements have been carried out over a wide range of frequencies from 5 MHz to 10 mHz using HIOKI HiTester LCR meter 3532-50 (50 Hz to 5 MHz) and 3522-50 (10 mHz to 50 Hz) at ambient condition having 25°C temperature and 35% relative humidity. The real, imaginary impedance and phase angles have been obtained from the EIS measurements. Moisture content has been estimated using Metler Tolado HS 153 Moisture Analyser. Linear sweep voltammetry (LSV) was performed using Agilent B2901A Precision Source/Measure Unit for analysing the electrochemical stability.

3 Results and discussion

3.1 Conductivity as a function of salt concentration and temperature

Impedance is measured by varying frequencies over an entire range of 10 mHz to 5 MHz. The Nyquist plots for salt concentrations from 0.4 to 2 g are shown in Figure 2, with an expanded view of higher salt/starch ratio in the inset.

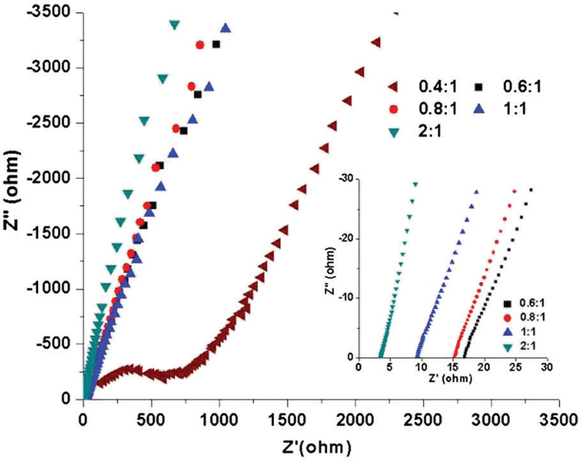

Figure 2: Nyquist plot for prepared materials having different salt/starch ratio (salt/starch ratios mentioned in the curve).

For lower salt concentration of 0.4 g, semicircle appeared in higher frequency region with tilted spike in lower frequency region, whereas, no such semicircle is obtained for higher salt concentrations. The semicircle indicates the parallel RC combination, whereas the straight line at ~90° to Z′ axis indicates the true capacitive behaviour and fast ion diffusion in the electrode-electrolyte interface (39). The dc resistance (R) is determined by higher frequency intercept with the Z′ axis which is decreasing with increase in salt concentration (40,41). Conductivity is calculated using this value of R with the help of equation:

$$\sigma = l/(AR) \tag{1}$$

where R is the bulk resistance of the sample given by the real axis (Z′) intercept of nyquist plot, l and A are the thickness and contact area of electrolyte. Figure 3 gives the variation of conductivity with salt concentration. The highest conductivity observed was ~3.43 × 10^{-2} S/cm for 2:1 salt/starch ratio.

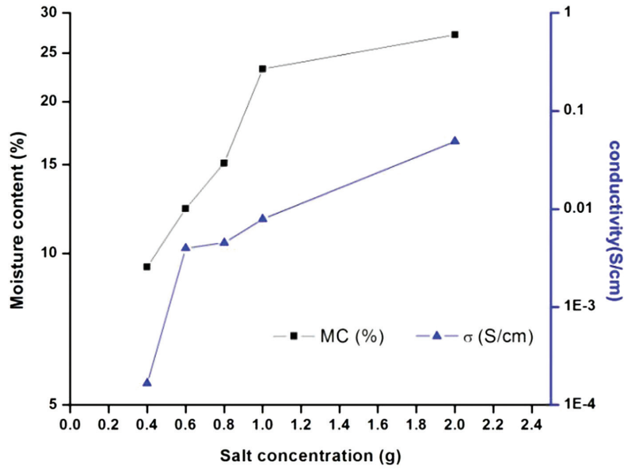

Figure 3: Variation of conductivity (σ) and moisture content (MC %) with salt concentration.

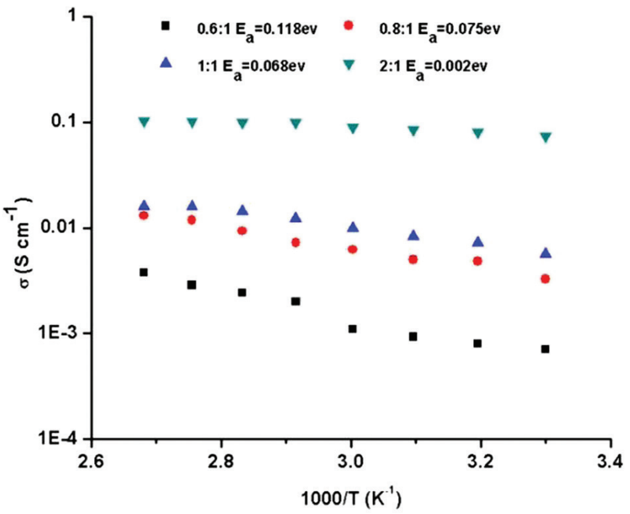

Figure 4: Temperature dependence of the conductivity for different salt/starch ratio. Respective activation energies are mentioned in the figure.

The conductivity is seen to be increasing with increasing salt concentration indicating plasticization behaviour of salt and increasing amorphicity of the system. Salt breaks the bigger starch molecules into smaller molecular weight starch molecules (42) hence increasing the amorphicity and water absorbing capacity of starch. The studied series covers the composition range from salt-in-polymer electrolytes (SIPE) to polymer-in-salt electrolytes (PISE). In PISE range where amount of salt is much higher than amount of polymer chances of polymer going in crystalline phase becomes very remote. The materials thus become flexible and softer with increasing salt content. Moisture content of the material is measured as a function of salt concentration and same is given in Figure 3. Moisture content follows the conductivity trend with varying salt concentration. Temperature dependence of conductivity is studied and linear variation of σ versus 1000/T is obtained for temperature range of 30°C to 100°C, as shown in Figure 4. Temperature has nominal effect on conductivity, and at higher salt concentration it remains almost independent of temperature. Although due to straight line nature of curves, thermally active arrhenius type process (43,44) seems to be prevailing in the system but authors will prefer not to give a confirmatory remark as the studied temperature range is not sufficiently wide to differentiate between Arrhenius and Vogel-Tammann Fulcher (VTF) (which is observed in amorphous material) type of phenomenon. Activation energy is calculated considering arrhenius type of behaviour and is mentioned in the figure. Since the conductivity is almost independent of the temperature hence a stable ambient behaviour of device is predicted when prepared material is used as electrolyte.

The aim of present study is to get an electrolyte for electrochemical device fabrication and hence 0.4:1 salt/starch ratio is not included in further study as its conductivity is too low to be considered as good electrolyte for device fabrication.

3.2 Bode phase and magnitude plots

Bode plots are the graphs of frequency response of phase angle and impedance magnitude. Phase angle indicates (45) whether equivalent circuit is dominantly capacitive, resistive or inductive. The capacitive nature is dominating when cell has phase angle close to -90°. Bode phase curves for different salt concentrations are given in Figure 5a. The highest phase angle (~-79°) is observed for sample having 2 g salt which approximately retains its value in wide frequency range (10 Hz to 10 kHz).

Frequency ($f_{-45°}$) corresponding to -45° is a figure of merit for comparative study of different samples. Table 2 summarises the value of $f_{-45°}$ for studied salt concentrations. As the salt concentration increases $f_{-45°}$ also shifts towards higher frequency side and the highest value is ~17 kHz. Phase angle tends to have a positive value beyond the frequency limit of ~1 MHz which indicates inductive behaviour at higher frequency which is described as undesired pseudo-inductance.

Bode magnitude plot is shown in Figure 5b. The inductive behaviour at higher frequencies and capacitive behaviour at lower frequencies results in resonance in the magnitude plot where both the components cancel each other giving purely resistive impedance. f_r the resonance frequency is the upper limit of frequency up to which device can be used for capacitive performance, after this

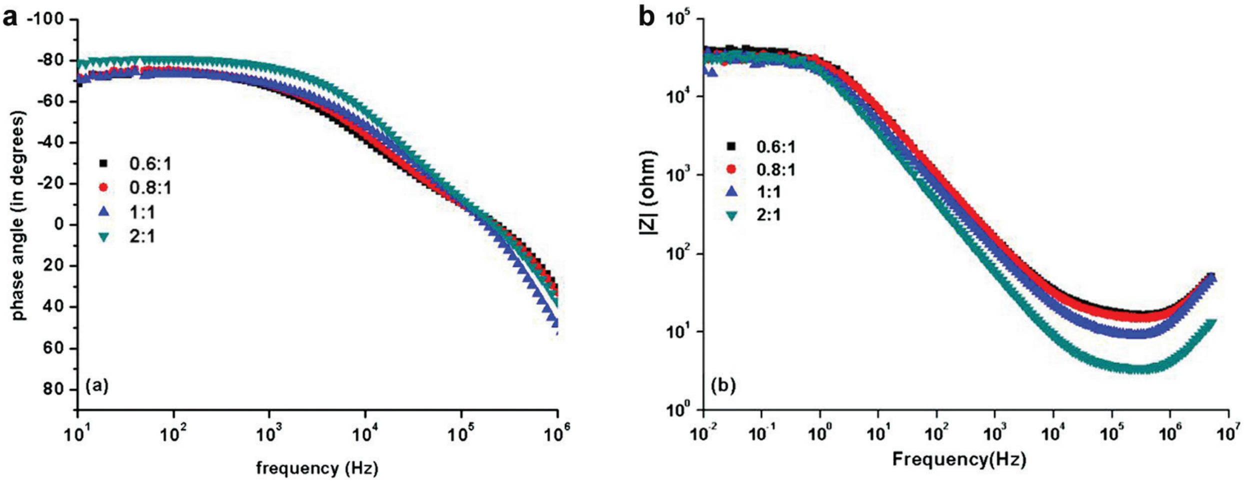

Figure 5: (a) Bode phase plot for materials having different salt/starch ratio; (b) Bode magnitude plot for materials having different salt/starch ratio (salt/starch ratio is mentioned in the curve).

Table 2: Values of various electrochemical parameters of different salt/starch ratio samples in 1 g of starch.

Amount of salt (g)	Conductivity (S/cm)	ESR (Ω)	$f_{-45°}$ (Hz)	τ (μs)	C_p (μF)	ESW (volt)	Phase angle (degree)
0.6	6.15×10^{-4}	16.9	7425	147	1.3	4.6	-68
0.8	8.00×10^{-3}	15.3	9369	105	1.4	4.5	-70
1.0	2.61×10^{-2}	9.4	11820	88	1.8	4.5	-73
2.0	3.43×10^{-2}	3.4	16760	75	2.7	4.5	-79

frequency pseudo-inductance dominates. f_r shows slight variation with salt concentration in present case and its value for all salt/starch ratio is approximately maintained to 0.1 MHz.

The value of Z at f_r gives the equivalent series resistance. The ESR values are also summarized in Table 2. ESR is strongly affected by salt concentration. For 2:1 salt/starch ratio it is quite low (~3.4 Ω). It should be remembered here that the thickness of the sample is 0.8 mm and for device fabrication it can be reduced to desired value using different techniques such as spin coating etc. This confirms its potentiality for electrochemical device fabrication.

3.3 Electrochemical stability, relaxation time and polarization behaviour

Electrochemical stability window is an important parameter to determine the quality of any energy storage device and a high ESW helps in achieving a high energy density (10). For supercapacitor application, the energy density ($E = CV^2/2$) depends upon square of electrochemical stability window (V) and hence is an important characteristic of electrolyte. It is estimated from linear sweep voltammetry (LSV) experiment where current is monitored as a function of voltage. For studied four systems, LSV curves are given in Figure 6. ESW is found to be ~4.5 V for all the samples. This is of the order of ionic liquids (46) which is a costly material and is liquid whereas the prepared material is of low cost and flexible free standing film. Hence for supercapacitive application point of view it is a very promising material.

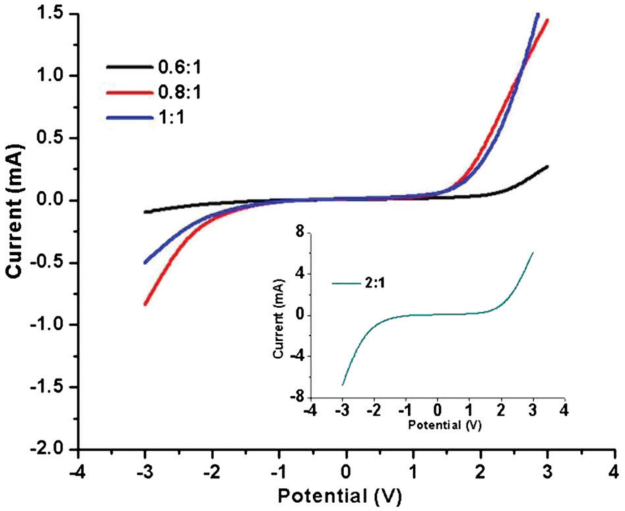

Figure 6: LSV plot for all the four samples (salt/starch ratios mentioned in the curve).

Another important parameter is ion relaxation time, which is estimated from variation of capacitance with frequency. Capacitance has different representations in literature. It is generally identified as a complex quantity (47) represented as:

$$C(\omega) = C' - jC'' \tag{2}$$

where C′ and C″ are real and imaginary components, given by:

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2}$$
$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \tag{3}$$

where, ω is the angular frequency, Z′ and Z″ are the real and imaginary parts of the impedances respectively.

C′ represents the utilizable capacitance of the system when measured at low frequency alternating current and its variation with frequency is shown in Figure 7a. C″ represents the energy dissipation i.e. dielectric loss and C″ vs. frequency plot is shown in Figure 7b.

The dielectric relaxation time, τ_0 is defined as the minimum time required to discharge all the energy from the device with efficiency >50% (48). τ_0 can be estimated from this plot by taking the inverse of the frequency corresponding to maximum value of C″ (49). Authors would like to emphasize that relaxation time of supercapacitor depends upon two different time periods i) time required for ions to reach at the electrode surface and ii) time required for ions to reach the inmost electrodes. τ_0 for 2:1 salt/starch ratio is found to be 75 µs and such a small τ_0 indicates that the prepared electrolyte matrix facilitates ion movement in a much better way in comparison to other electrolytes. τ_0 decreases with increasing salt concentration indicating faster ion transport at higher salt concentration, which can be co-related with higher moisture content facilitating easier ion transport. Smaller relaxation time makes it a potential candidate for the supercapacitor fabrication, as it insures the faster delivery of charge resulting in greater pulse power. The relaxation peak sharpens with increase in salt concentration indicating distribution of relaxation processes. The difference in moisture content at different salt concentration may be the reason of distribution in relaxation process because at low moisture content starch matrix assisted charge transport may also exist whereas at higher moisture content water molecule assisted ion transport may be dominating.

The other representation of capacitance includes series (C_s) and parallel (C_p) capacitance. The series and parallel capacitance of the material is calculated using the following formulas:

$$C_s = -(\omega Z'')^{-1}$$
$$C_p = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \tag{4}$$

As obvious that C_p and C′ are same and it gives the utilizable capacitance (50) of the device, whereas C_s gives the total capacitance of the system. The ratio of C_p and C_s is the parameter determining the polarization behaviour of the system, ideally the ratio should be equal to unity (51,52). The variation of C_p/C_s with frequency is shown in Figure 8a, which is observed to be approximately equal to 1 for all the salt/starch ratios and maintained for a broader frequency range. The value of the ratio is maintained to be ~0.96 for frequency range of 10 Hz to 2321 Hz for 2 g concentration, followed by other samples of lesser salt concentrations with slightly less broad frequency range.

A better picture of overall performance of the system may be obtained by observing the C(R) plots for the

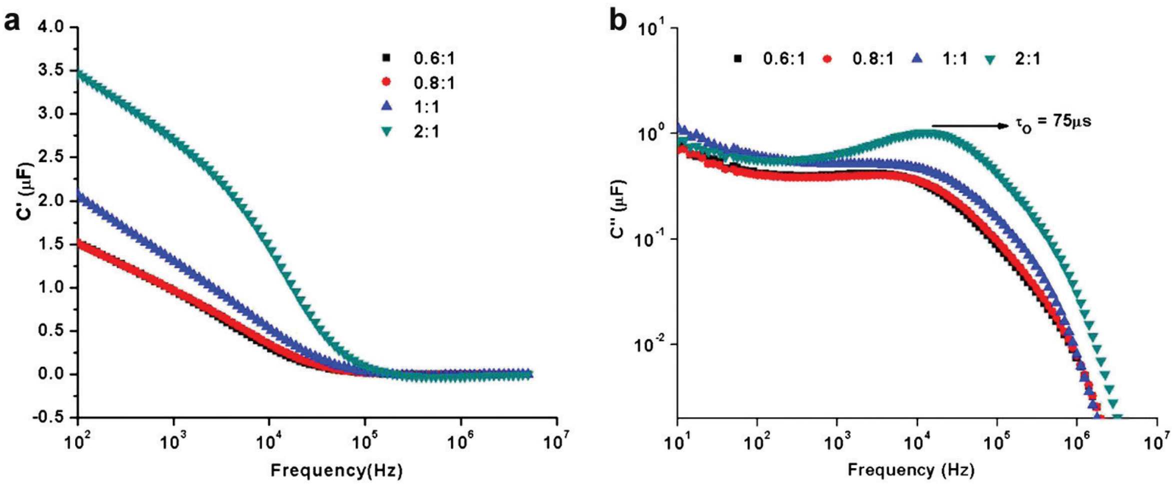

Figure 7: (a) Variation of C′ with frequency; (b) Variation of C″ with frequency for different materials (salt/starch ratio mentioned in the curve).

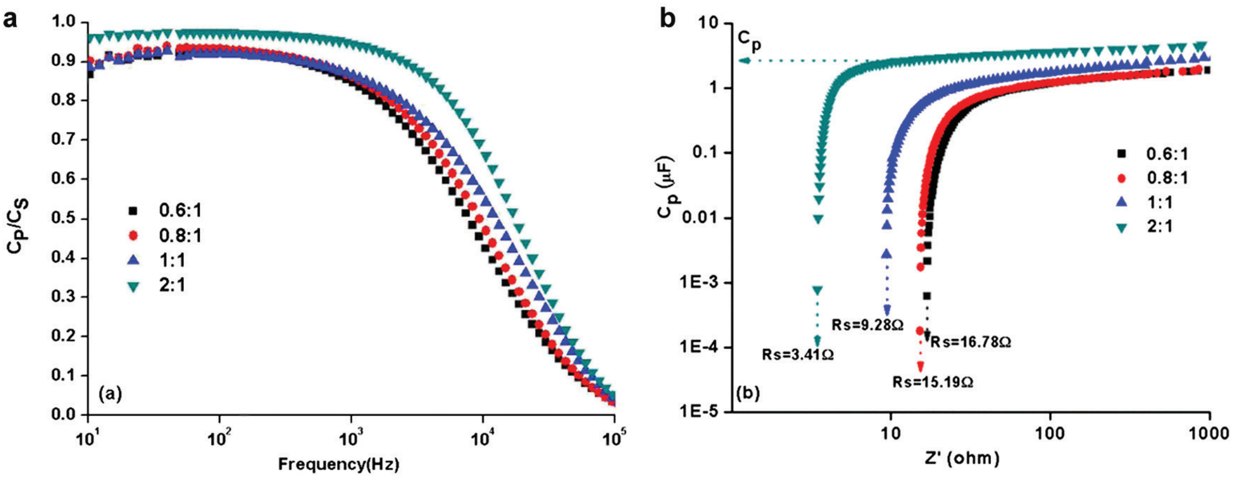

Figure 8: (a) C_p/C_s ratio variation with frequency; (b) Variation of C_p with Z′ (salt/starch ratios mentioned in the curve).

Table 3: Comparison of studied electrolyte with the high conducting synthetic polymer (PMMA and PVA) based electrolyte having magnesium salt.

Polymer + salt	Conductivity (S/cm)	ESW (V)	Activation energy (eV)	References
Potato starch + $MgCl_2$ (300 wt% salt)	3.43×10^{-2}	4.6	0.002	Studied Electrolyte
PMMA + $Mg(ClO_4)_2$ (15 wt%) + 2:1 EC:PC ratio	3.13×10^{-3}	.....	0.18	(53)
PMMA + $Mg(CF_3SO_3)_2$ (20 wt%) + 2:1 EC:PC ratio	1.27×10^{-3}	.....	0.19	(53)
PMMA + $Mg(CF_3SO_3)_2$ (60 wt%) + 1:1 EC:PC ratio	6.08×10^{-4}	.....	0.18	(54)
PMMA + PC + $Mg(ClO_4)_2$	1.59×10^{-2}	.....	0.2	(55,56)
PMMA + Mg triflate (60 wt%) + 2:1 EC:DEC ratio	5.58×10^{-5}	4.8	0.11	(57)
PAN + PC + EC + $Mg(CF_3SO_3)_2$	1.80×10^{-3}	5	0.13	(58)
PAN + MgI_2 (60 wt%)	1.9×10^{-3}	.....	0.11	(59)
92.5 PVA + 7.5 PAN + $Mg(ClO_4)_2$ (25 wt%)	2.94×10^{-4}	3.65	0.21	(60)
PAN (18 mol%) + EC:PC (64 mol% : 14 mol%) + $Mg(ClO_4)_2$ (4 mol%)	3.2×10^{-3}	.....	0.24	(61)

determination of characteristics of performance of a capacitor. Plot of C_p vs. Z′ for different salt/starch ratio is shown in Figure 8b. DC capacitance is calculated from the logarithmic scale representation of C_p vs. Z′ curve from the line parallel to Z′ axis as marked in figure. The highest DC capacitance value (~2.7 μF) is for 2:1 salt/starch ratio with other samples having almost closer values. The ESR value is determined by extrapolating the curve to intersect the Z′ axis, with the smallest ESR value (3.41 Ω) of the highest salt containing sample.

4 Conclusions

Potato starch being naturally abundant and easy electrolyte preparation technique make it an interesting option as future electrolyte materials. In Table 3 a comparison of studied electrolyte with the high conducting synthetic polymer based electrolyte having magnesium salt is given (53-61). The present system does not have any plasticizer still its conductivity (~3.43×10^{-2} S/cm) is higher and its ESW (4.6 V) is comparable to summarized electrolytes. Hence the studied system is an easy to prepare, low cost and benign to environment. Synthesis is via solution casting hence it can be easily synthesized in different shapes and sizes giving an edge to designing ease. It is flexible electrolyte with very low relaxation time and low ESR value. The above behaviour makes the studied system a promising option for future device fabrication.

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Compliance with ethical standards: The authors declare that they have no conflict of interest.

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