Development of Nanocomposite Polymer Electrolytes (NCPEs) in Electric Double Layer Capacitors (EDLCs) Application

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OVERVIEW

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2) Problem Statement
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4) Methodology
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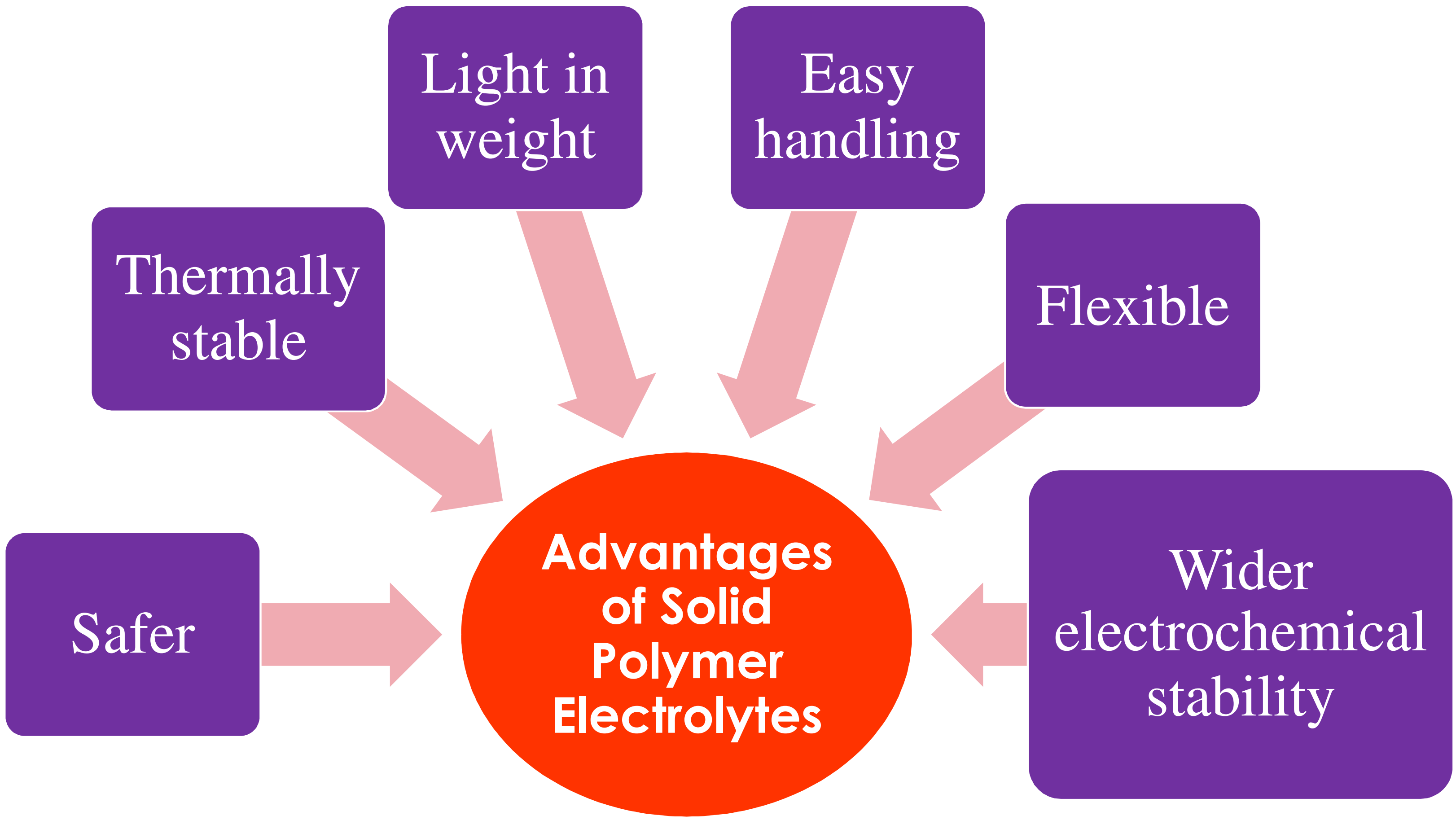
INTRODUCTION


Light in weight
Easy handling
Thermally stable
Flexible
Safer
Advantages of Solid Polymer Electrolytes
Wider electrochemical stability

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Applications of Polymer Electrolytes

Lithium ion batteries

Sensors

Fuel cells

Solar cells

Supercapacitors

Electrochromic windows

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PROBLEM STATEMENTS

Low ionic conductivity

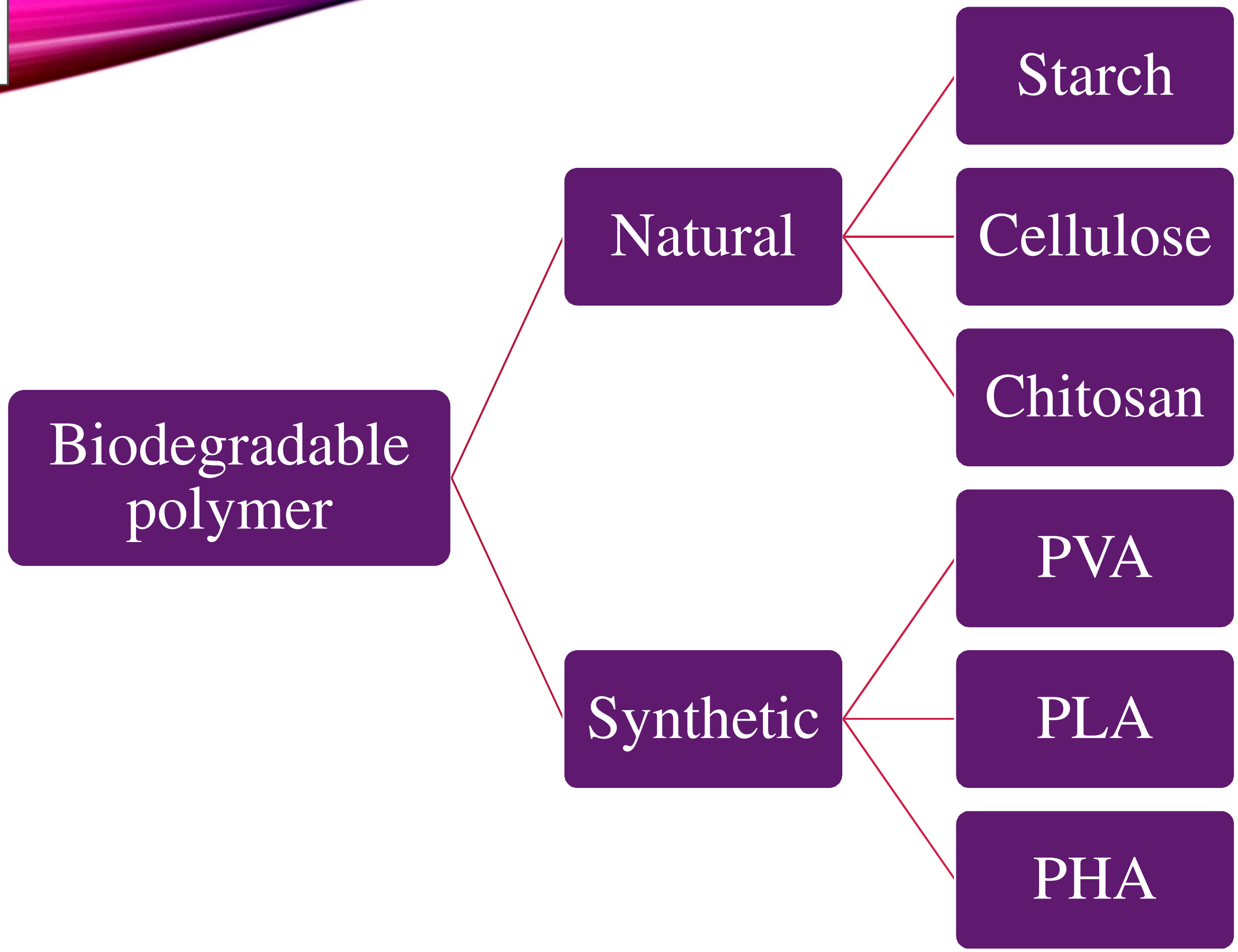
- Polymer blending
- Mixed salt system
- Mixed solvent system
- Ionic liquids
- Plasticizers
- Fillers

Environmentally unfriendly

- Biopolymer
- Ionic liquids

Low mechanical strength

- Fillers
- Polymer blending


Biodegradable polymer
Natural
Synthetic
Starch
Cellulose
Chitosan
PVA
PLA
PHA

LITERATURE REVIEW

Advantages of PVA

- Excellent tensile strength
- Non–toxic
- Good chemical stability
- Excellent thermal stability
- Biocompatible
- High dielectric constant
- Excellent charge storage capacity
- Environmentally friendly

Advantages of Ionic Liquids

- Wider electrochemical potential window
- Non–flammable
- Non–volatile
- Plasticizing effect
- High ion content
- Superior electrochemical stability
- Excellent thermal stability
- Non–toxic

Filler

Inorganic

Active

- Lithium–nitrogen (Li_2N)
- Lithium aluminate ($LiAlO_2$)
- Lithium containing ceramics
- Titanium carbides (TiC_x)
- Titanium carbonitrides (TiC_xN_y)

Passive

- Inert metal oxide
- Molecular sieves and zeolites
- Ferroelectric materials
- Rare earth oxide
- Solid superacid
- Carbon
- Nano–clay
- Heteropolyacid

Organic

- Graphite fibre
- Aromatic polyamide
- Cellulosic rigid rods (whiskers)

Advantages of Fillers

- Enhance interfacial stability
- Reduce T_g
- Increase cationic diffusivity
- Improve physical properties
- Decrease the crystallinity
- Enhance thermal stability
- Improve morphological properties
- Lower interfacial resistance
- Improve long–term stability
- Reduce water retention

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Supercapacitors

Pseudo–capacitors

Redox reaction

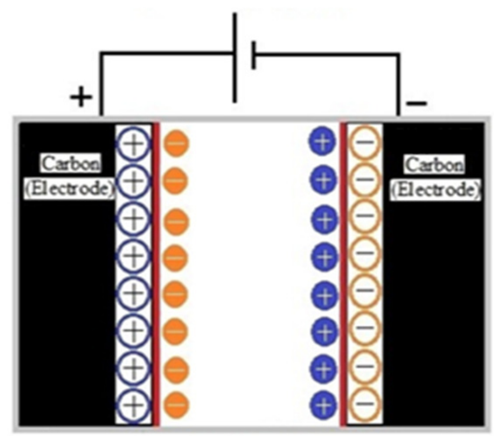
- Conducting polymers
- Metal oxide

Electric double layer capacitors (EDLCs)

Charge accumulation

- Carbon

Hybrid capacitors



Ion adsorption

ELECTRIC DOUBLE LAYER CAPACITORS (EDLCS)

- Longer cycle life
- Higher power density
- Higher capacitive density
- Faster charge–discharge rate
- Higher ability to be charged and discharged continuously without degradation
- Inexpensive

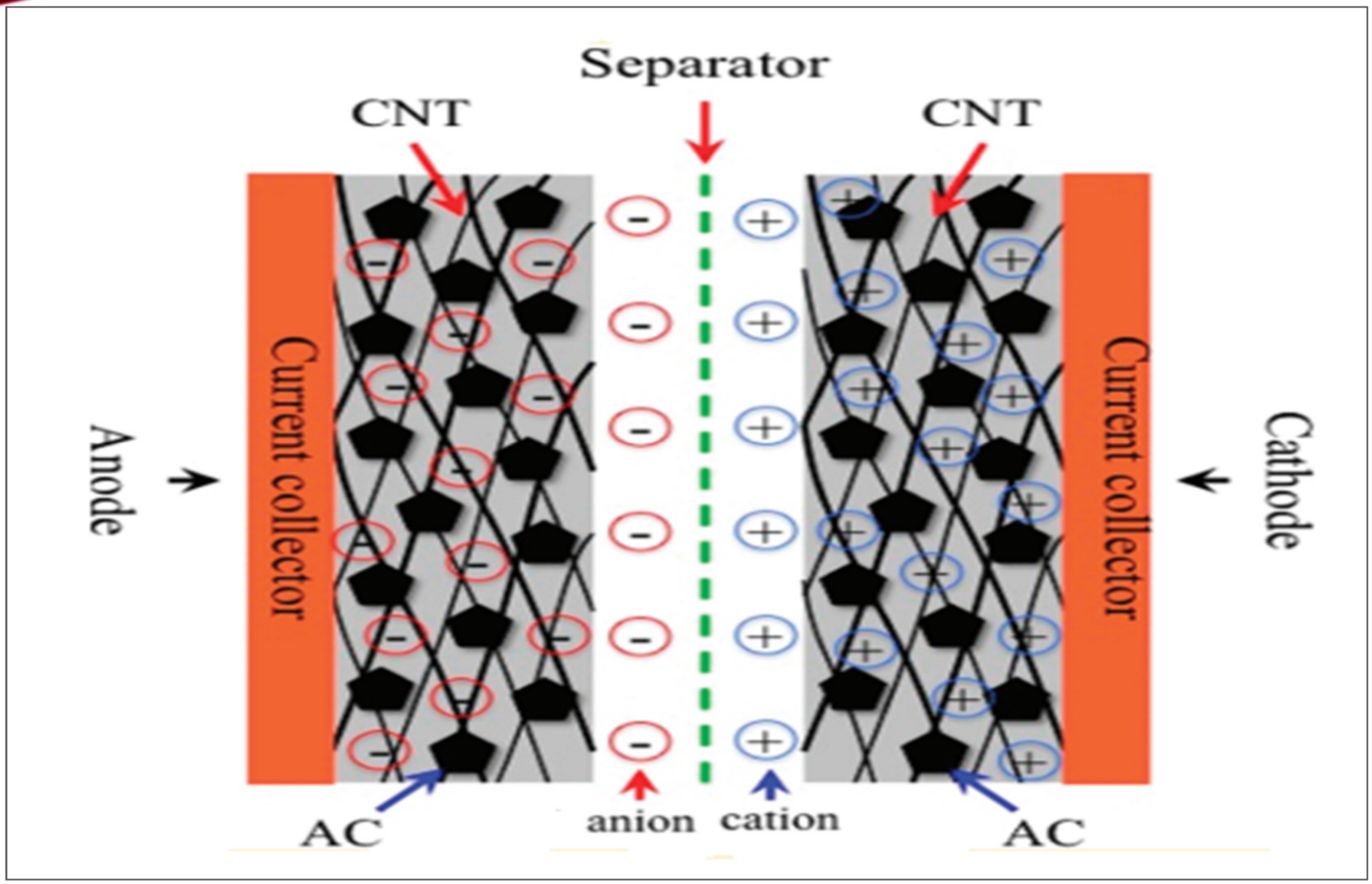
Disadvantages of AC

CNT

Hard diffusion

Limit the accessibility of charge carriers

High microporosity (pore dimension: <2nm)


Separator
CNT
CNT
Anode
Current collector
Current collector
Cathode
AC
anion
cation
AC

MATERIALS

MATERIAL	ROLE
Poly (vinyl alcohol) (PVA)	Polymer
1–butyl–3–methylimidazolium bromide (BmImBr)	Ionic liquid
Silica (SiO_2) (70nm) Titania (TiO_2) (40–50nm) Zirconia (ZrO_2) (<100nm) Alumina (Al_2O_3) (<100nm)	Fillers
Distilled water	Solvent

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METHODOLOGY

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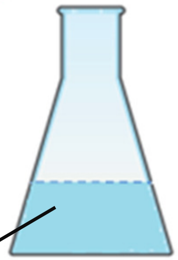
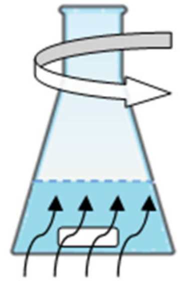
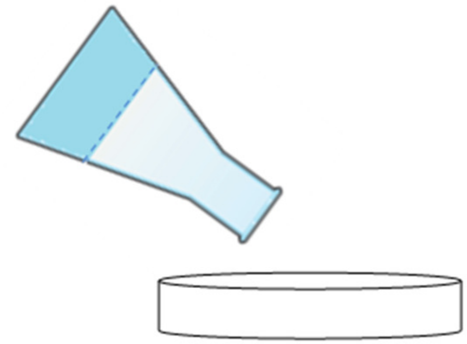
A) SAMPLE PREPARATION



PVA+ BmImBr+
$SiO_2/TiO_2/ZrO_2/Al_2O_3$



Stir and heat at 80 °C



Cast on Petri dish

- EIS
- DSC
- LSV

Al_2O_3

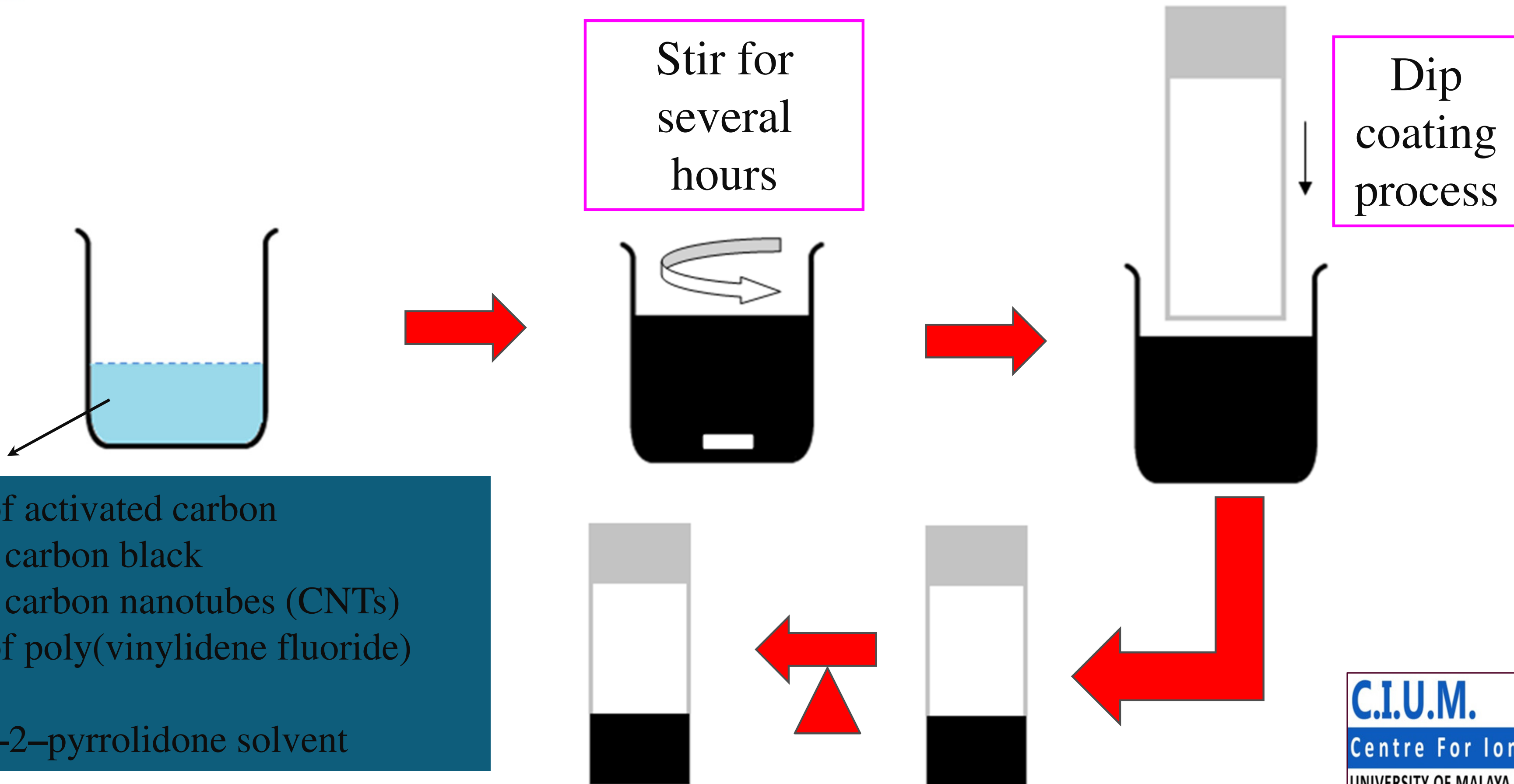
ZrO_2

TiO_2

SiO_2

Formation of free standing polymer electrolyte

B) ELECTRODE PREPARATION



80 wt.% of activated carbon
5 wt.% of carbon black
5 wt.% of carbon nanotubes (CNTs)
10 wt.% of poly(vinylidene fluoride) (PVdF)
1–methyl–2–pyrrolidone solvent

C) EDLC FABRICATION & CHARACTERIZATION

Configuration: electrode/polymer electrolyte/electrode

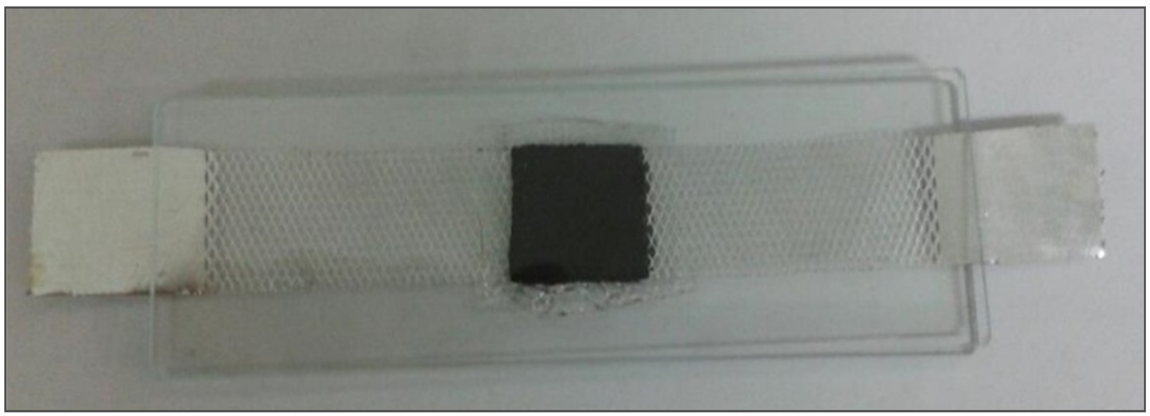


Figure 1: The fabricated EDLC using the highest conducting ionic liquid–added polymer electrolyte from each system.

- ***Cyclic Voltammetry (CV)***
- ***Galvanostatic Charge–Discharge (GCD)***

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RESULTS AND DISCUSSION

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Ambient Temperature–Ionic Conductivity Studies

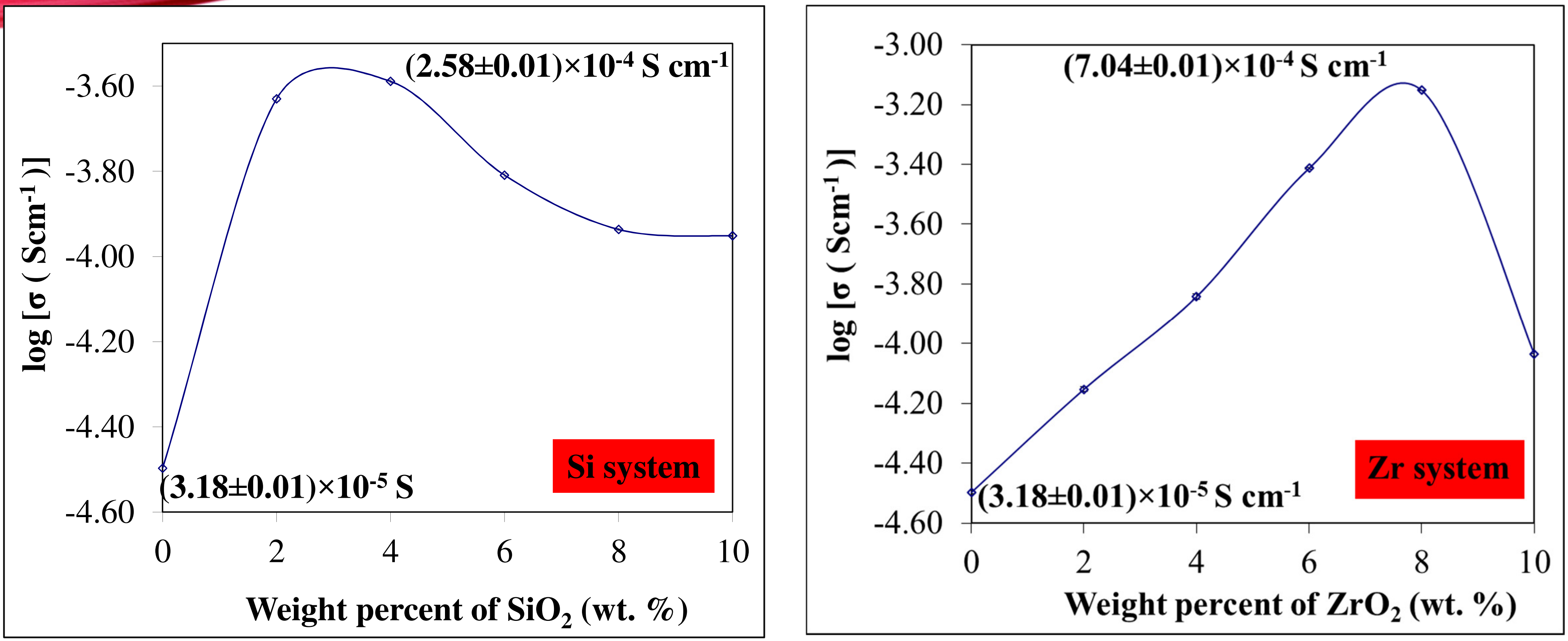

Figure 2: The logarithm of ionic conductivity of polymer electrolyte at different mass fraction of (a) SiO_2 and (b) ZrO_2.

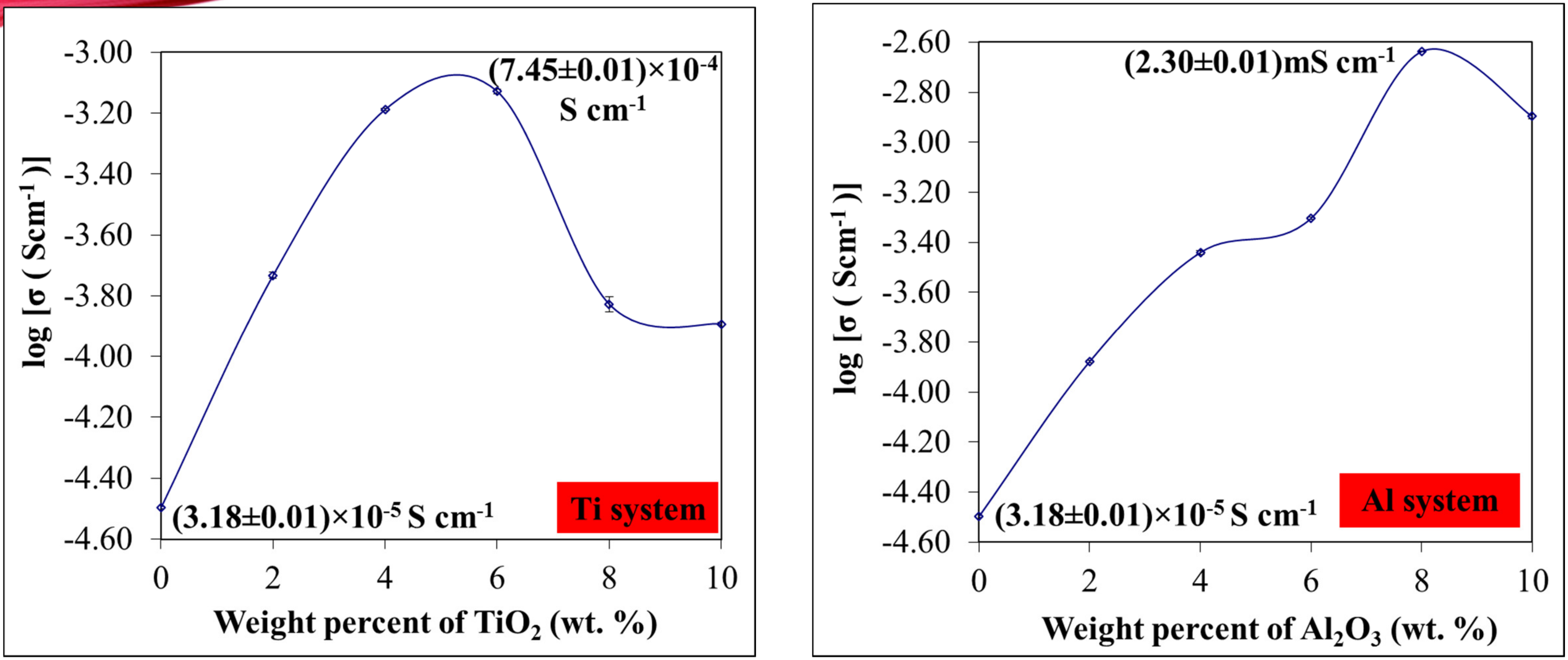

Figure 3: The logarithm of ionic conductivity of polymer electrolyte at different mass fraction of (a) TiO_2 and (b) Al_2O_3.

Temperature Dependent–Ionic Conductivity Studies

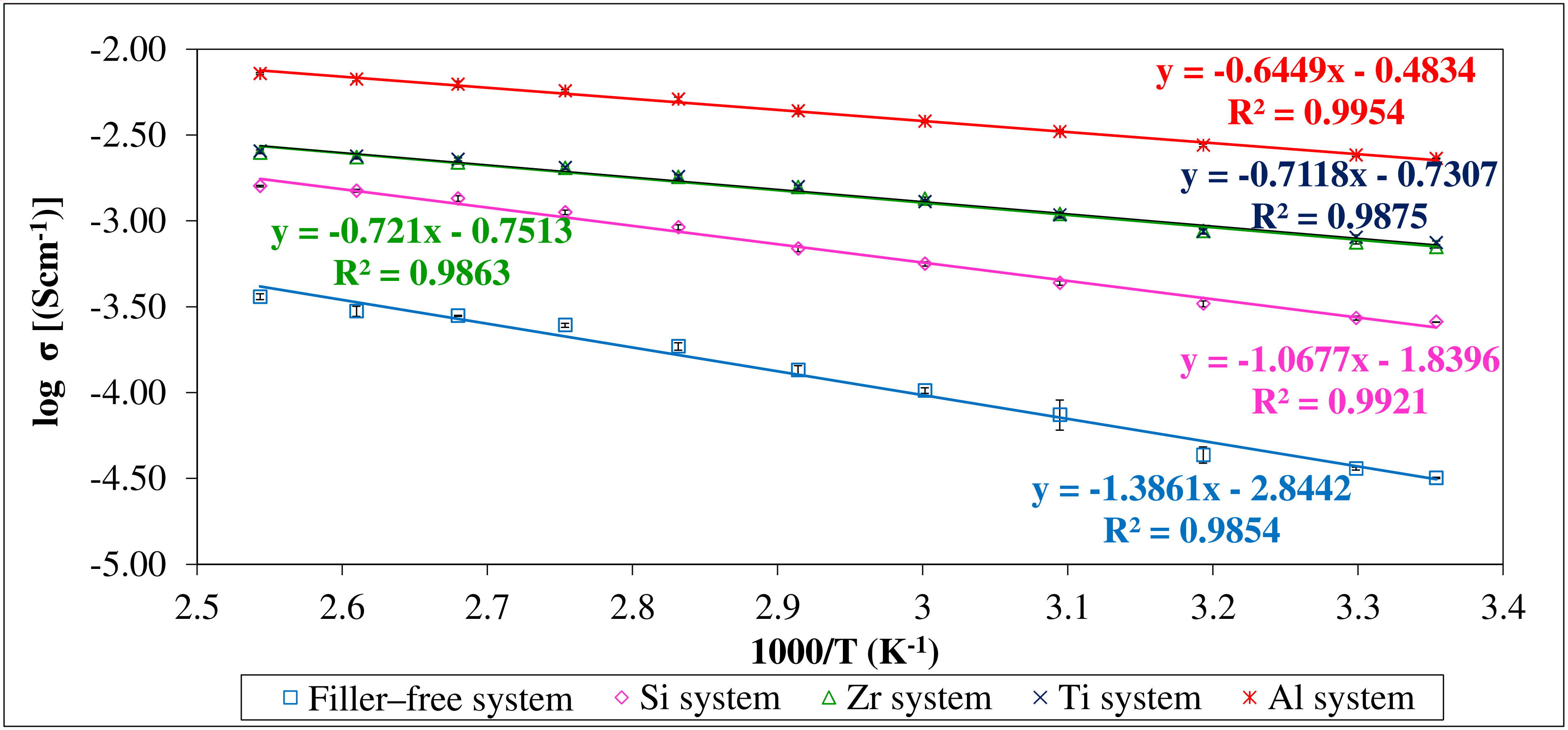

Figure 4: Arrhenius plot of filler–free polymer electrolyte and filler–doped NCPEs.

Sample	Activation energy, E_a (eV)	Log A	Pre–exponential constant, A
Filler–free system	0.2751	–2.8442	1.43×10^{-3}
Si system	0.2119	–1.8396	0.0145
Zr system	0.1431	–0.7513	0.18
Ti system	0.1413	–0.7307	0.19
Al system	0.1280	–0.4834	0.33

Differential Scanning Calorimetry (DSC)

T_g

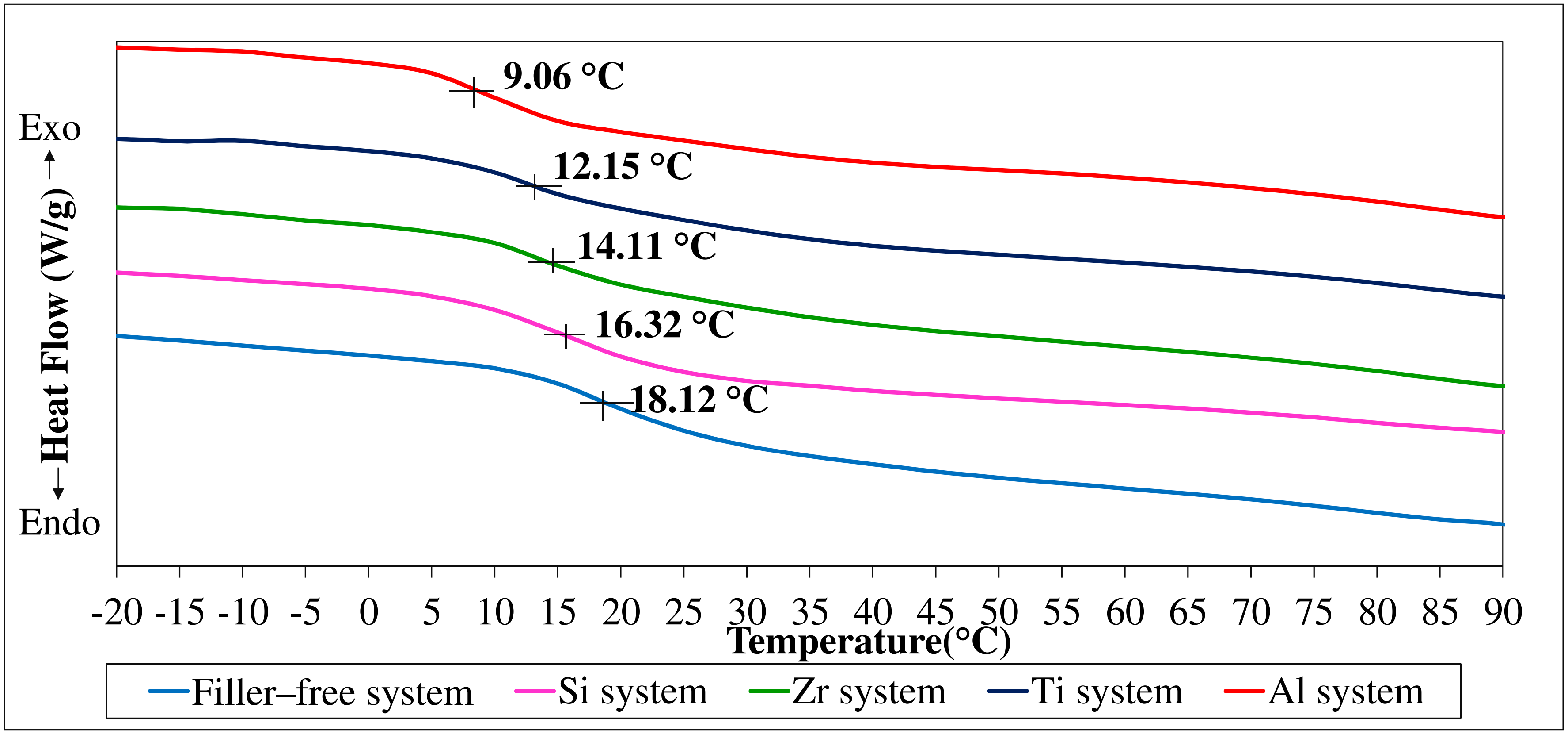

Figure 5: Glass transition temperature (T_g) of polymer electrolytes.

T_m

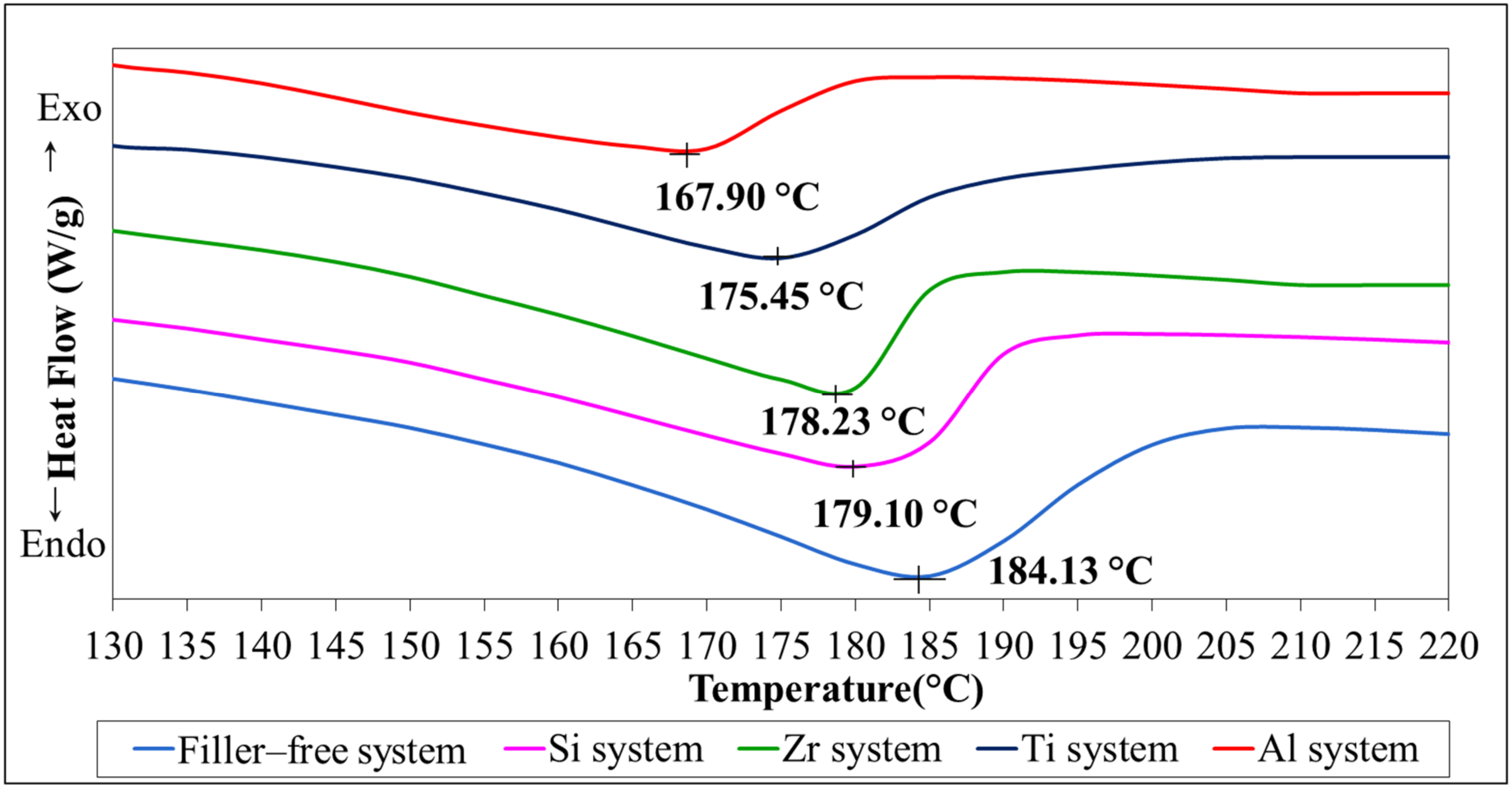

Figure 6: Crystalline melting temperature (T_m) of polymer electrolytes.

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T_c

$$X_c = \frac{\Delta H_m}{\Delta H_m^{\theta}} \times 100\%$$

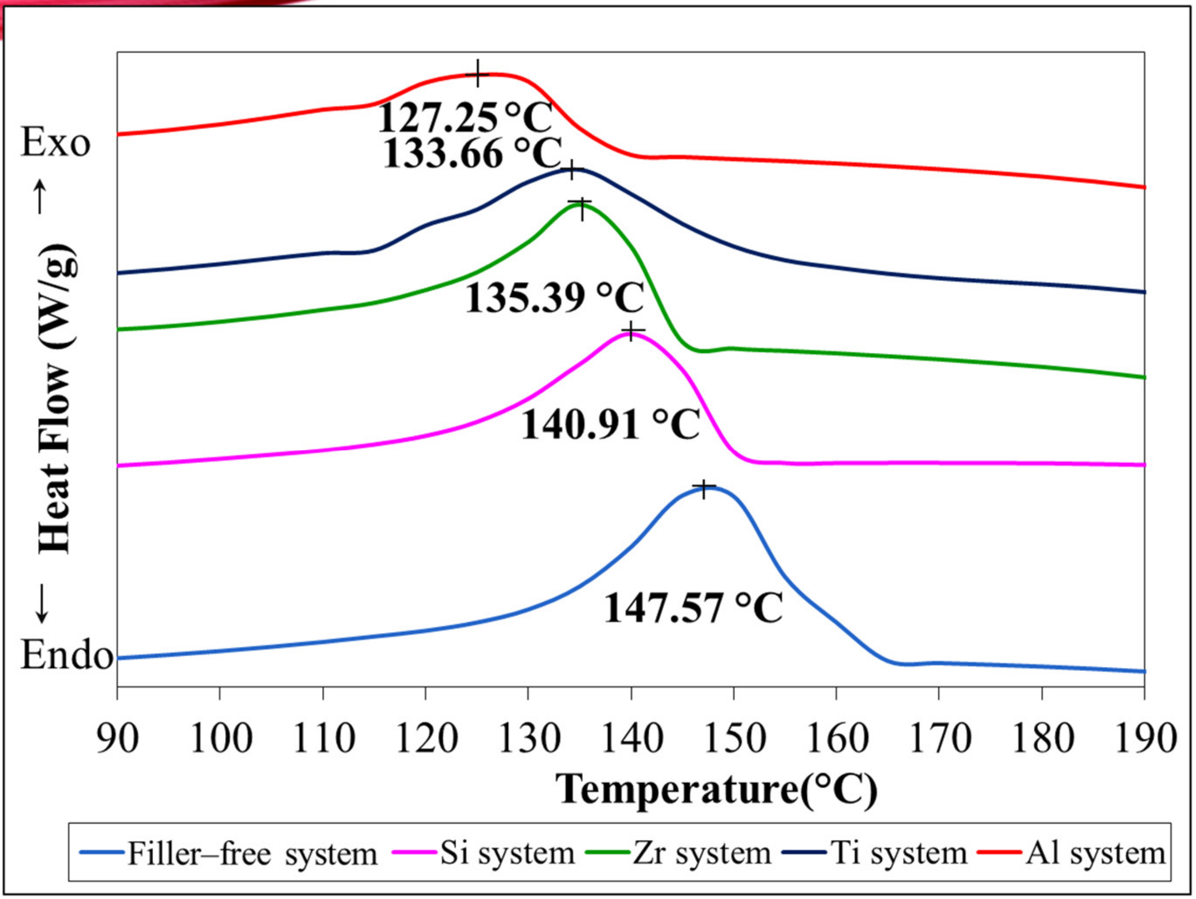


Figure 7 : Crystallization temperature (T_c) of polymer electrolytes.

	Heat of Fusion (Jg^{-1})	Relative crystallinity (%)
Filler–free system	719.7	100
Si system	358.7	50
Zr system	287.6	0.40
Ti system	217.1	0.30
Al system	203.3	0.28

Linear Sweep Voltammetry (LSV)

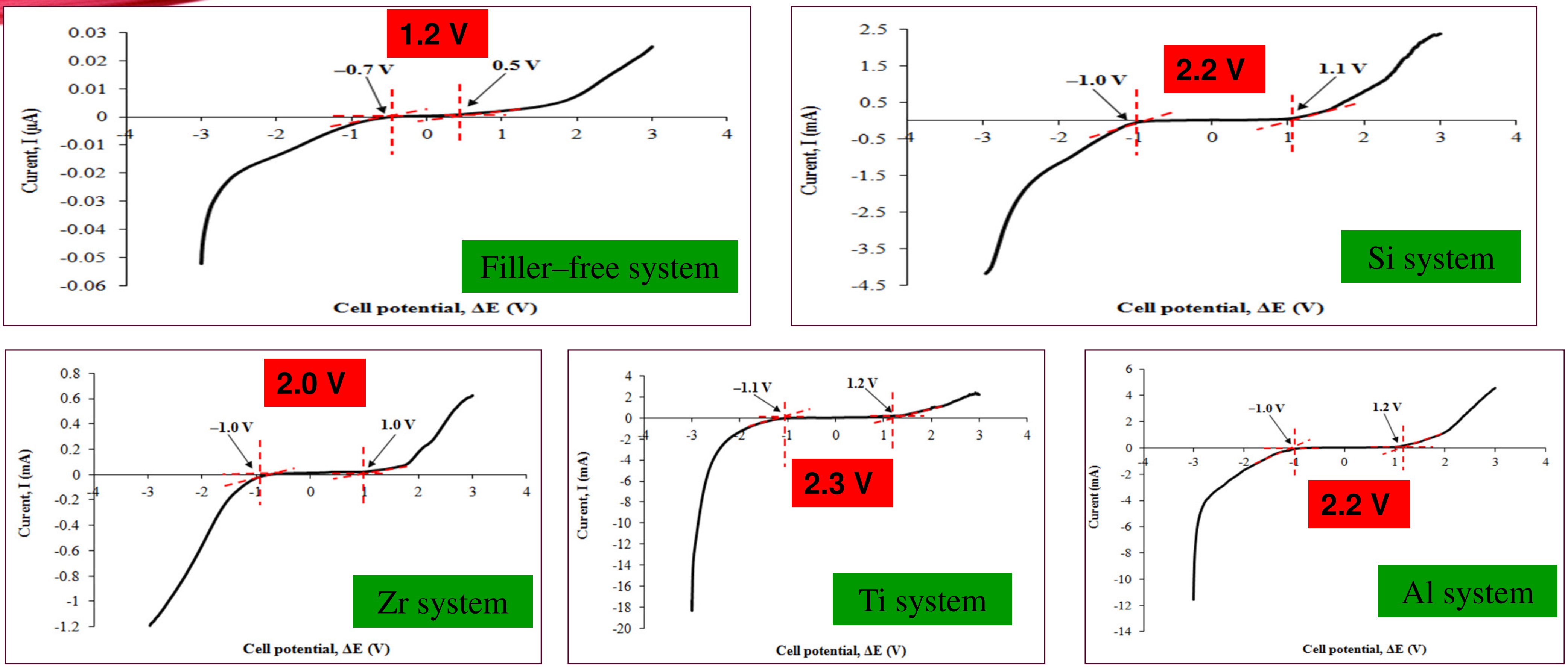
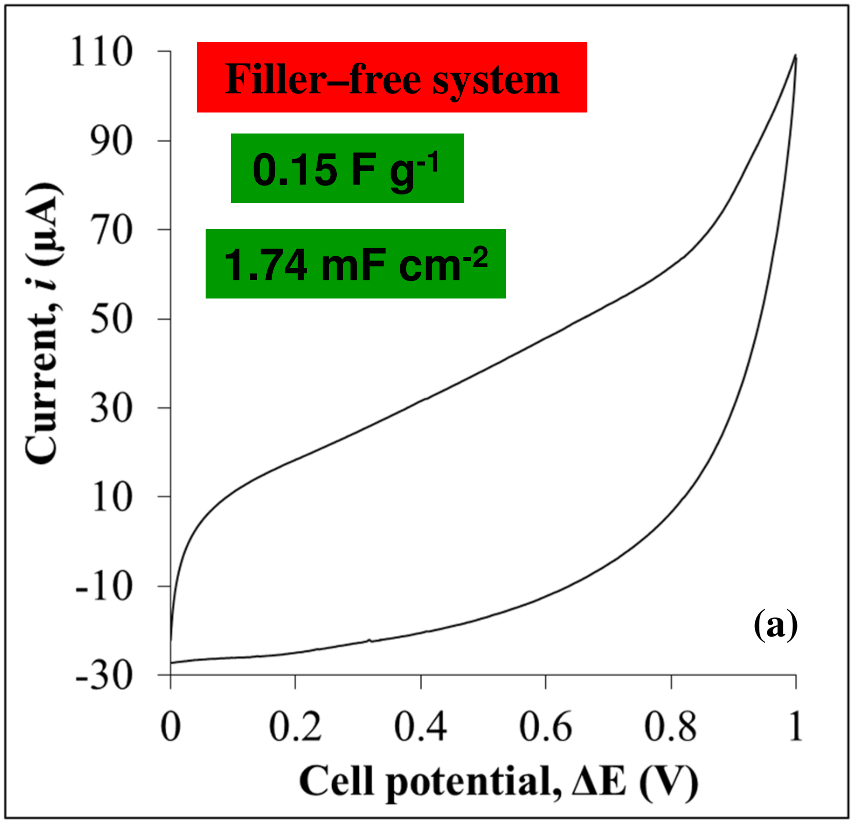


Figure 8: LSV response of the most conducting polymer electrolyte from each system.

Cyclic Voltammetry (CV)



$$C_{sp} = \frac{i}{sm}$$

$$C_{sp} = \frac{i}{sA}$$

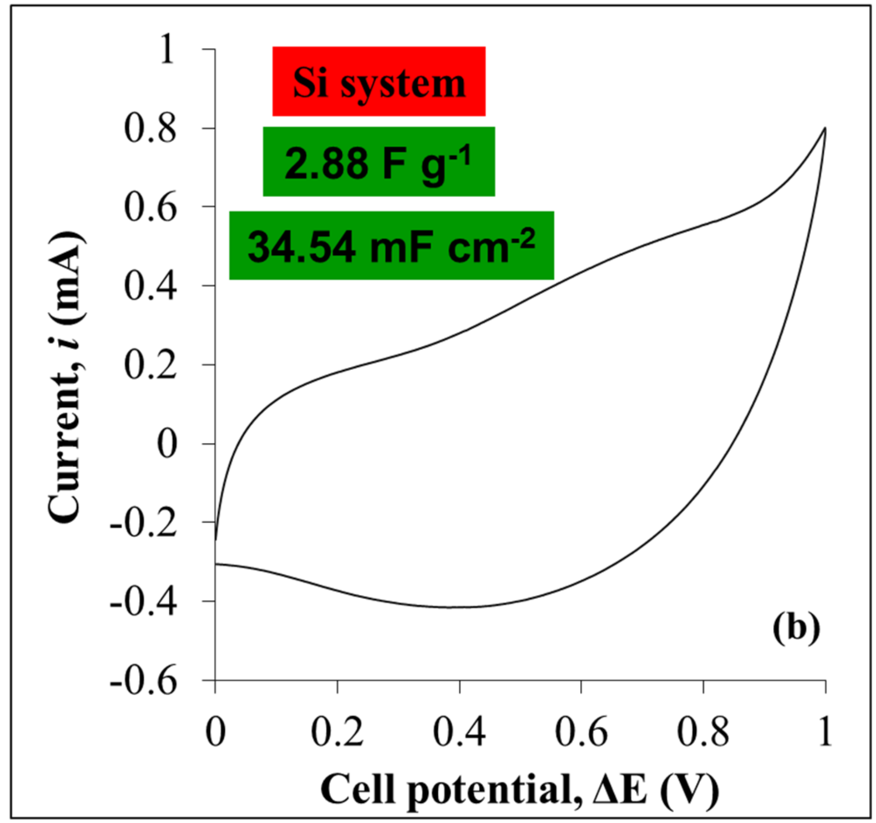


Figure 9: Cyclic voltammogram of EDCL containing the most conducting polymer electrolyte from (a) filler–free system and (b) Si system.

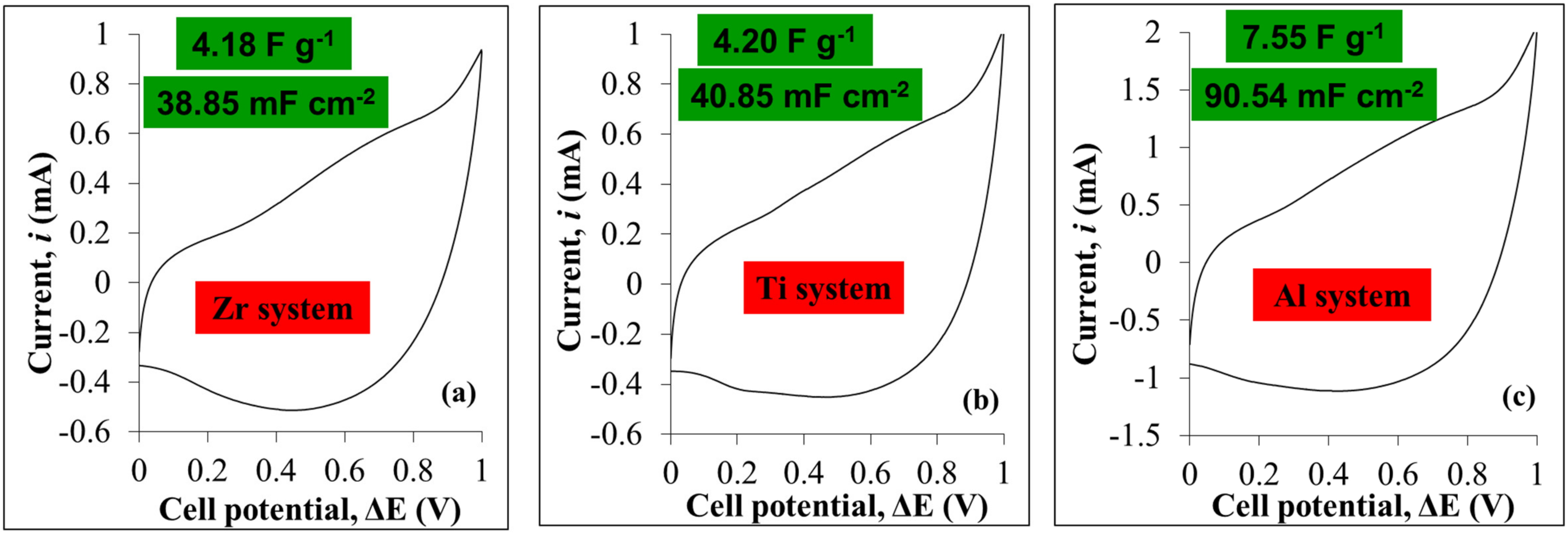
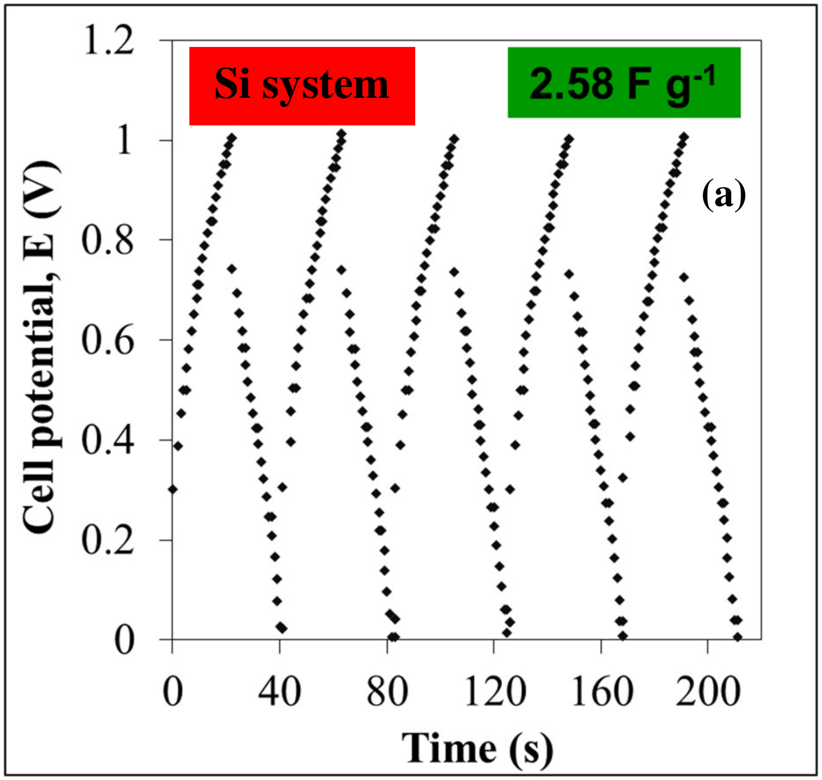


Figure 10: Cyclic voltammogram of EDCL containing the most conducting polymer electrolyte from (a) Zr system, (b) Ti system and (c) Al system.

Galvanostatic Charge–Discharge Analysis (GCD)



$$C_{sp} = \frac{I}{m\left(\frac{dV}{dt}\right)}$$

$$E = \frac{C_{sp} \times (dV)^2}{2} \times \frac{1000}{3600}$$

$$P = \frac{I \times dV}{2 \times m} \times 1000$$

$$\eta = \frac{t_d}{t_c} \times 100$$

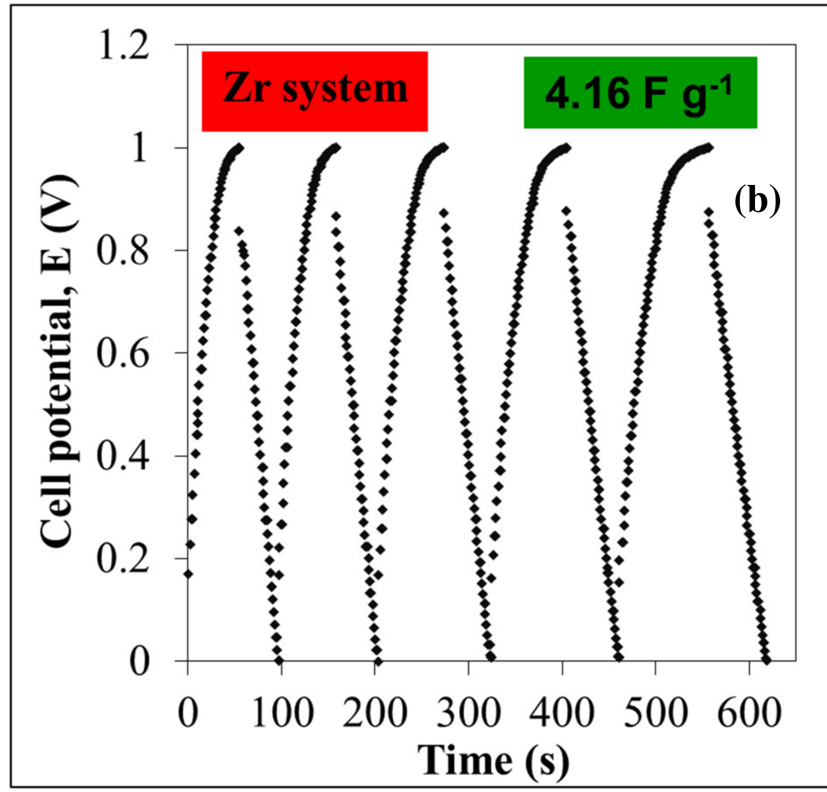


Figure 11: Galvanostatic charge–discharge performances of EDLC containing (a) Si system and (b) Zr system over first 5 cycles.

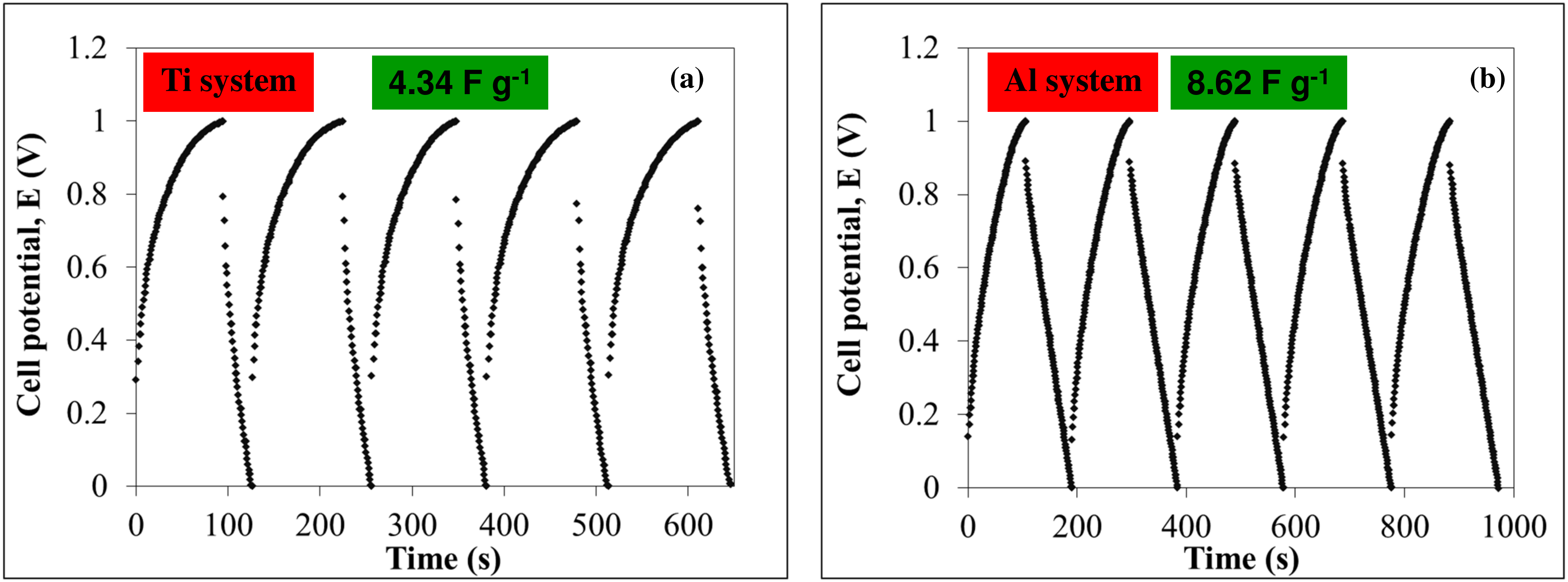


Figure 12: Galvanostatic charge–discharge performances of EDLC containing (a) Ti system and (b) Al system over first 5 cycles.

System	Specific discharge capacitance, C_{sp} ($F\ g^{-1}$)	Coulombic efficiency, η (%)	Energy density, E ($W\ h\ kg^{-1}$)	Power density, P ($W\ kg^{-1}$)
Si system	2.58	86	0.18	34.94
Zr system	4.16	40	0.36	36.76
Ti system	4.34	76	0.42	38.41
Al system	8.62	81	0.95	41.15

CONCLUSIONS

- Addition of nano–sized fillers
  - Increases the ionic conductivity
  - Follows Arrhenius rules for the conduction mechanism
  - Reduces the Tg and crystallinity
  - Improves the electrochemical stability window
  - Enhances the electrochemical properties of EDLCs (i.e. capacitance)
- Alumina–based polymer electrolyte is a good choice as separator in EDLC

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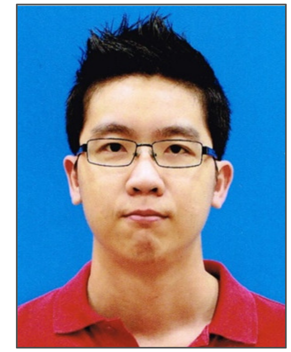
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Alumina-based polymer electrolyte