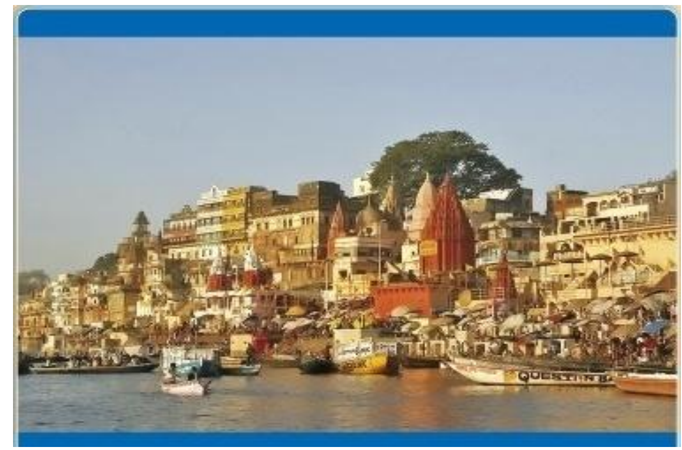
Ionogel electrolytes for rechargeable lithium batteries



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Plan of presentation

1. Introduction

2. Ionic liquid based ionogel polymer electrolytes

3. Ionogels obtained due to immobilization of Ionic Liquids in porous/ordered porous matrices for rechargeable lithium batteries

4. Summary

Introduction

- Limited life span of fossil fuels
- Global warming: supression of CO_2 (transportation sector occupies about 24% of energy consumption and also ~ 20% of CO_2 discharge)
- Energy storage systems for running vehicles/ hybrid electric vehicles required
- Intermittent alternative energy sources, as well as electric transportation require convenient energy storage systems, e.g., high energy density lithium rechargeable batteries etc.

Lithium Batteries

Further R&D is still required to improve the performance to meet the HEV-EV requirement, **safety**, **energy density etc.**

The rechargeable Li batteries use electrolytes based on organic carbonates EC, PC etc. which poses a serious safety risk and strongly reduces battery operative temperature range.

Ionic liquid (IL) based electrolytes due to nonflammability and high ionic conductivity are emerging as novel and safe electrolytes. To overcome the problems like leakage. Corrosion etc with the liquid nature ILs are impregnated in polymeric membranes/porous matrices

Ionogel based on gel polymer electrolytes

Solid polymer electrolytes (SPEs) are commonly obtained by complexing a polar polymer (like polyethylene oxide, PEO) with an ionic salt ($LiPF_6$, $LiBF_4$, LiTFSI etc).

Various approaches such as (i) *Changing the length of polymer chain (or mol. wt).* (ii) *Using* easily dissociable ionic salts (salts having large anion) (iii) Using *Plasticizers to reduce the crystallinity* (iv) *Composite formation by dispersing filler particles* (v) Use of "*ionic liquids*" have been adopted to enhance the conductivity of SPEs suitable for lithium polymer polymer battery (LPB) and for obtaining good thermal and mechanical stability (which improves the performance of batteries)

ILs act as supplier of charge as well as plasticizer.

Part II: Results: IL based ionogel polymer electrolytes based rechargeable cells

Electrolyte and cathode preparation

Poly (ethylene oxide), PEO or P(VdF-HFP)

Lithium salt LiTFSI/LiFSI

Mixed in suitable solvents and stirred for 3 hours

Added desired amount of ionic liquid, [PYR13][TFSI]

Stirred again for longer time

Viscous solution of Polymer+salt+ionic liquid

Vacuum drying for 24 hours at 10^{-5} torr

Free standing IL based polymer electrolyte films (50-150 micron thick)

10 wt% polyvinylidene fluoride (PVdF) + N-methyl-2-pyrrolidonel

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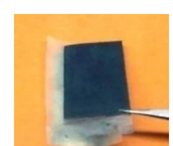
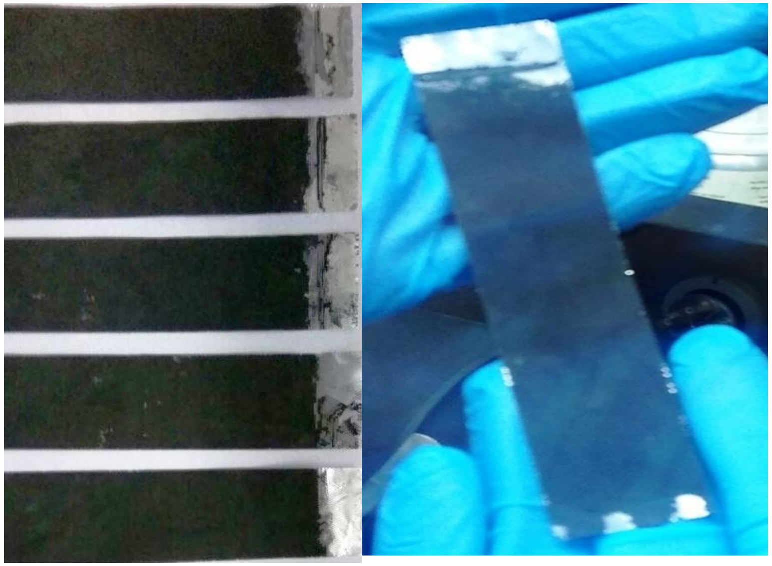
Drying at ambient condition

Vacuum dried at 110^{o}C for 48 hours



Cell preparation and its working

Meshed Al sheet



Meshed Al sheet coated with Cathode $LiFePO_4$ (2.5x6.5 cm^2)

Electrolyte PEO+20% LiFSI +7.5% EMIMFSI (3x7 cm^2)

Li foil

Cu foil

(few drops of ionic liquid+salt solution is spread on both sides anode-electrolyte as well as cathode-electrolyte interface)

Cells during working condition

Ionic and Cationic transport numbers

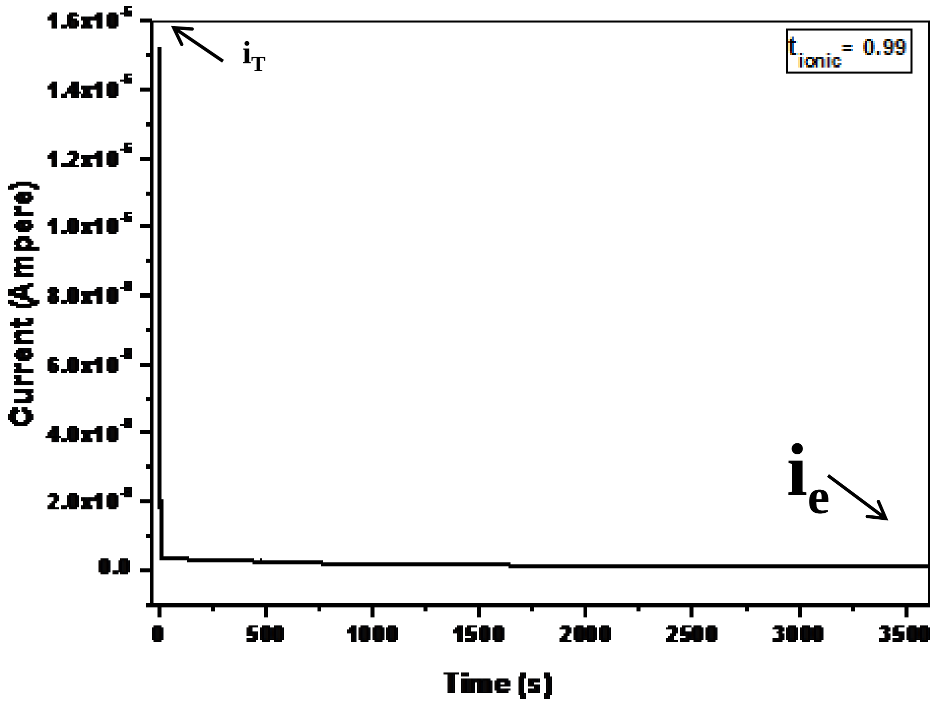


Fig. (a) DC polarisation curve of polymer electrolyte PEO + 20% LiTFSI + 30% IL sandwich between two symmetry stainless steel electrodes with applied voltage 10 mV.

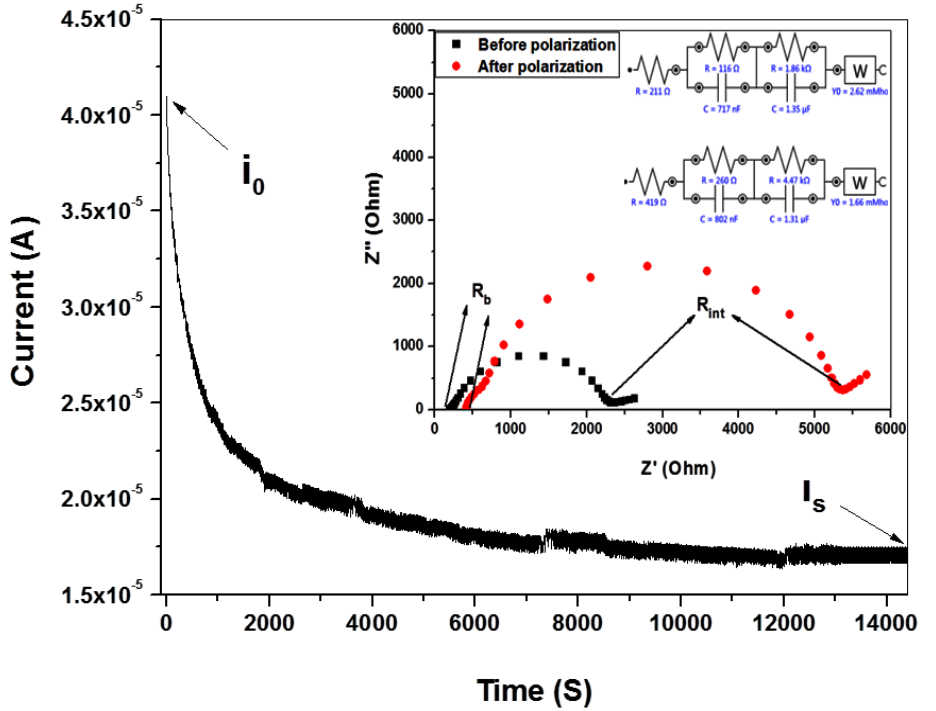


Fig. (B): dc polarization curve at the applied voltage (ΔV) of 0.1 V. Inset of Figure (B) shows the ac impedance plot, along with fitted circuit, before (R_0) and after (R_s) polarization of the cell (i.e. Li/PEO+20% LiTFSI+ 30% IL/Li) at 25 ^{0}C

- Total ionic transference number (t_{ion}) is calculated by using the relation:

$$t_{ion} = (i_T - i_e) / i_T$$

$t_{ion} \sim 0.99$

- Li^+ contribution in conductivity process is calculated by using the formula:

$$t_{Li+} = I_s.(\Delta V - I_0.R_0) / I_0.(\Delta V - I_s.R_s)$$

$t_{Li+} \sim 0.41$

Electrochemical study

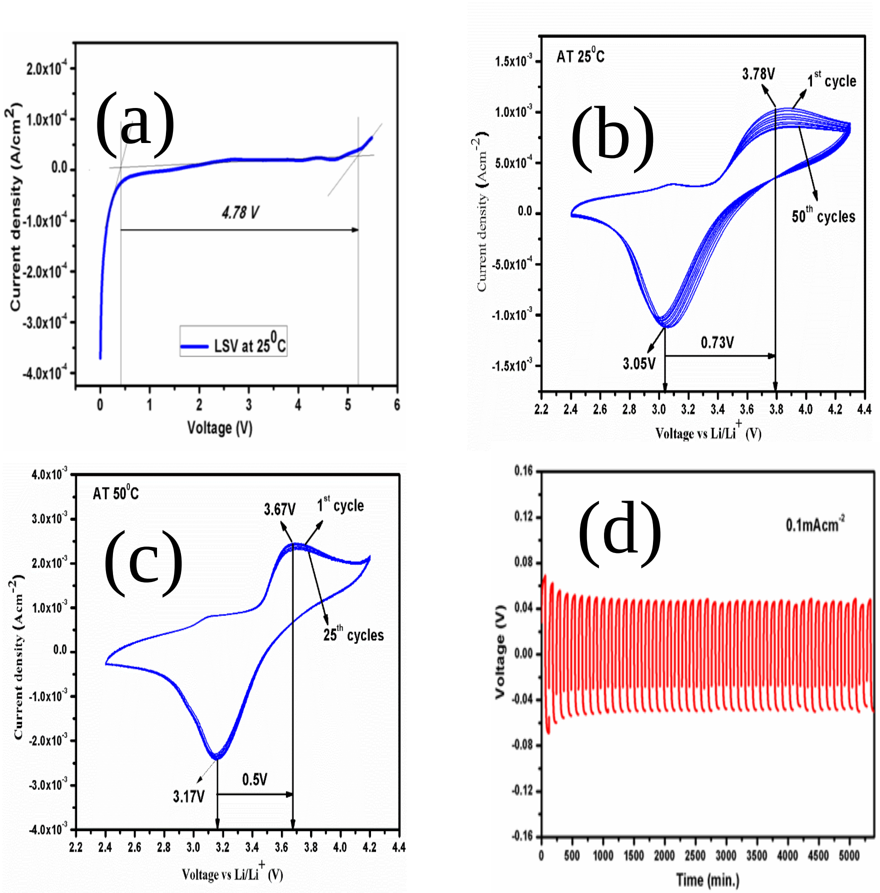


Fig. Linear sweep voltammetry (LSV) of the cell Li/40wt.% ILGPE/SS at 25 ºC (a), Cyclic voltammetry curves with scan rate 10 mV/s of the cell (Li/40wt.% ILGPE/$LiFePO_4$) at 25 ºC (b), at 50 ºC (c) and Lithium plating/stripping measurements of symmetric cell (Li/40wt.% ILGPE/Li) at room temperature (d).

The electrochemical stability window of ILGPE [(PVdF-HFP + 20 wt.% LiTFSI) + 40wt% EMIMFSI] is about 4.78 V.

Cycling performance of Li/$LiFePO_4$ cell

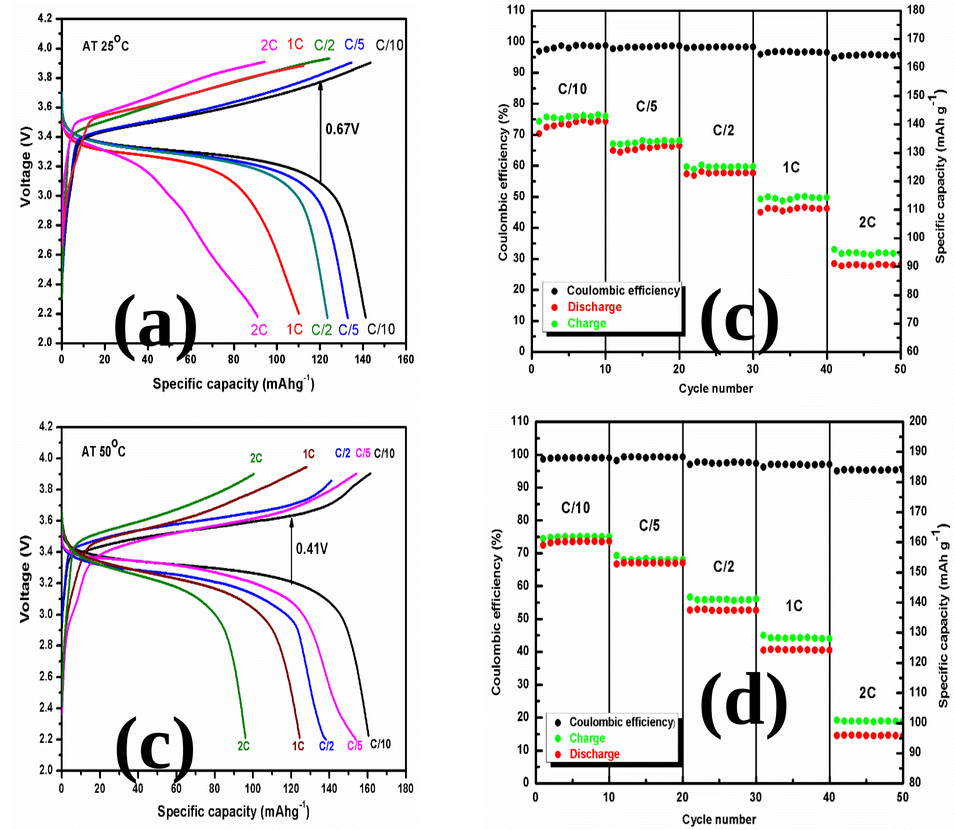
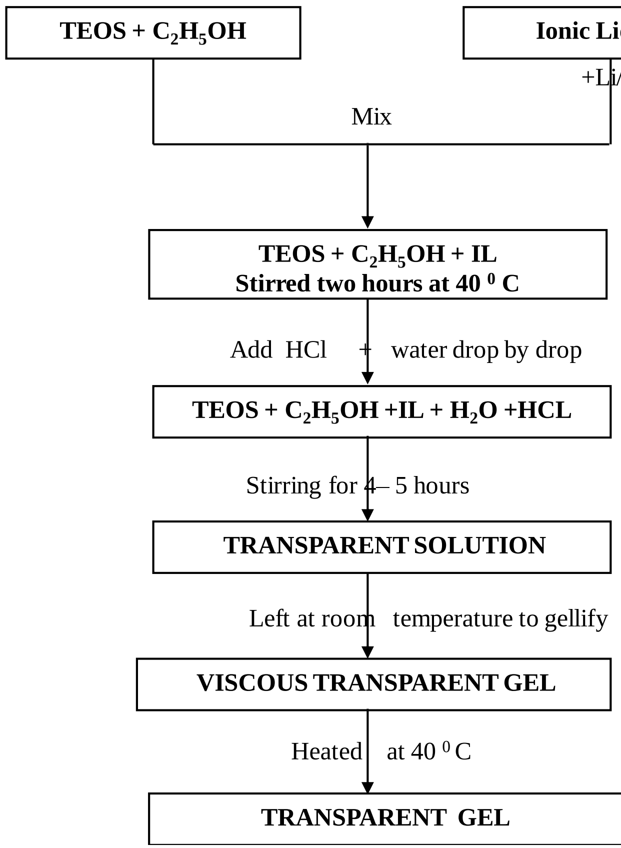


Fig. Galvanostatic charge-discharge profiles of the cell (Li/(PVdF-HFP + 20 wt.% LiTFSI) + 40wt% EMIMFSI /$LiFePO_4$) at various C-rates and different temperatures (a,b at 25ºC and c,d at 50ºC).

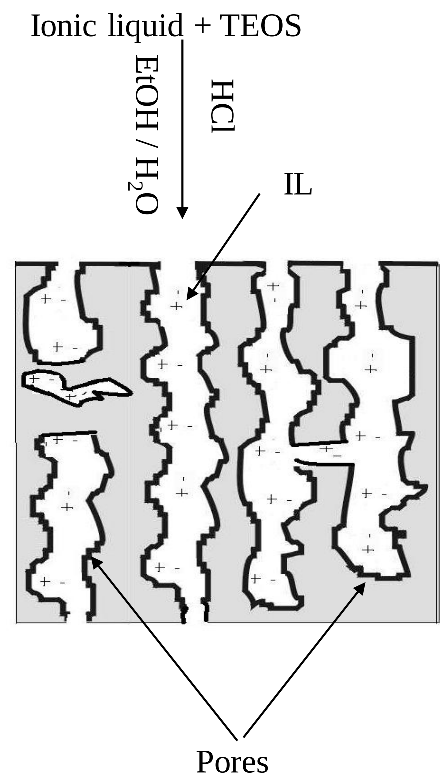
The open circuit potential of the prepared cell was found to be 3.2V.

Synthesis of Ionogels

I: Preparation of IL confined silica gel matrix



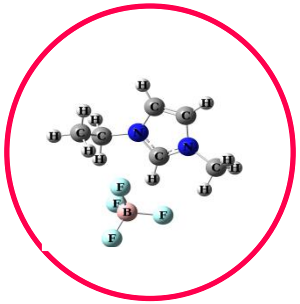
BMIM PF6



The porous matrices provide abundant channels to confine ILs while maintaining good mechanical properties.

Thermal, Electrical and Structural Behavior of Ionic Liquid Confined in Ordered Mesoporous MCM-41

Pore filling of MCM-41 matrix with IL (Ionogel)



Ionic liquid (1-ethyl-3-methyl imidazolium tetrafluoroborate; [EMIM][BF_4])

MCM-41

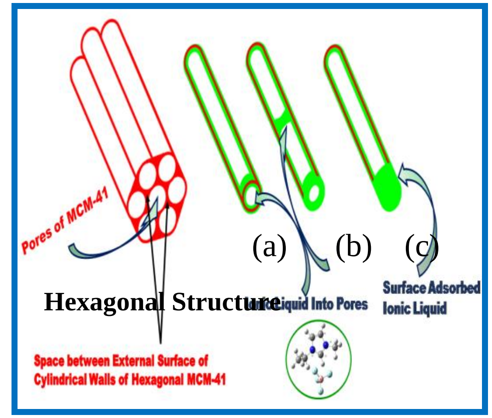
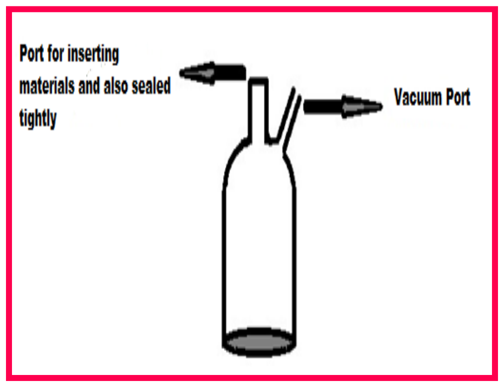


Fig. Various types of filling process (a) primary pore filling (b) increasing amount into pores (c) external surface adsorption on pore mouth.

In presence of methanol



Ultrasonicated for 30 min. and stirred for several hours

Different steps involved in preparation of ionogels

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Li rechargeable cell using MCM-41 ionogel electrolyte

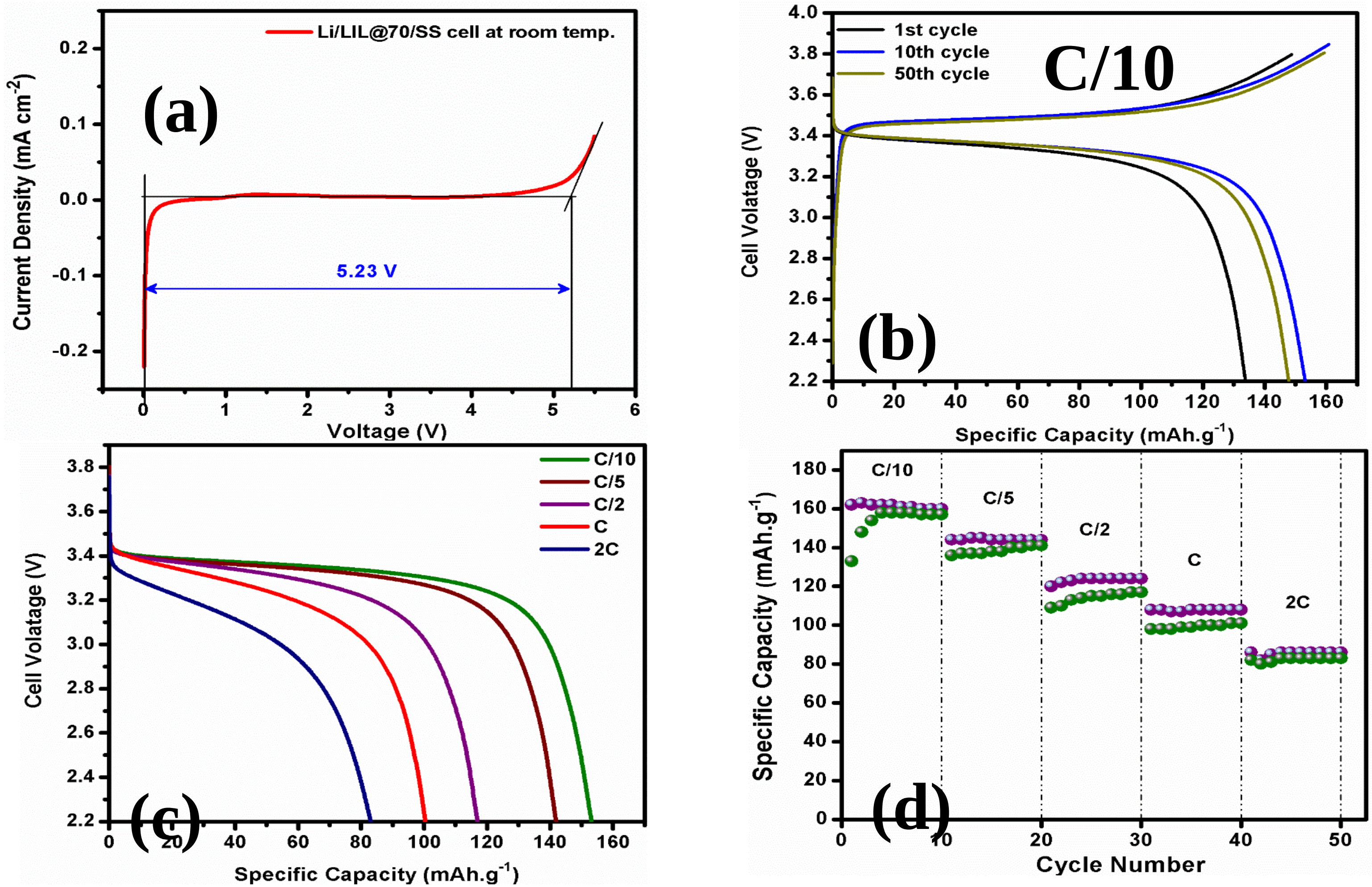

Fig. Electrochemical characterizations (a) LSV, (b) charge-discharge profile at C/10 rates, (c) and (d) different C-rates of Li/LIL@70/$LiFePO_4$ cell at room temperature.

*LIL@70 denotes 70wt.% of lithium salt-ionic liquid (LIL; LiTFSI+EMIMTFSI) solution with the molality of 0.6 mol/kg incorporated into MCM-41.

Summary of the talk

In brief, ionogel obtained by dispersing IL in polymer electrolytes/porous matrices is shown as a "novel route" to obtain good electrolytes for improved performance of rechargeable batteries.

Thanks