Chemically Cross-linked Polymer Gel Type Electrolyte for DSSCs

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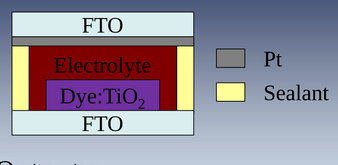
Abstract

Electrolyte for dye-sensitized solar cells is a type of solution that contains electrolyte ions dissolved in organic solvents. Organic solvent such as acetonitrile based liquid-state electrolyte is conventionally used for the fabrication of high conversion efficiency dye-sensitized solar cell (DSSC). However, the liquid-state electrolyte based DSSC always requires encapsulation resulting in additional process and fabrication cost, and its long-term stability issues such as leakage of electrolyte at high-temperature becomes serious obstacles for the commercialization. Recently, to overcome this problem, quasi solid- or gel-state electrolyte composed of polymer and electrolyte ions has been considered as an alternative for the liquid-state electrolyte. In this study, we have prepared chemically cross-linked gel-type polymer electrolyte using unique polymer, cross-linking agent and propylene carbonate as solvent by heating the polymeric mixture at an elevated temperature. Gel-type polymer electrolyte has been prepared by adding electrolyte ions to the polymer gel and let the ions absorb into polymer gel matrix for 24 hrs. We discuss the formation of gel-type polymer electrolyte as a function of time and temperature and analyze their characteristics. Finally, we fabricate DSSCs using those gel-type electrolytes and analyze their photovoltaic properties and long-term stability compared with that of DSSC using liquid-type of electrolyte.

Introduction

❑ Dye-Sensitized Solar Cells

- Low cost and simple process
- High efficiency
- Aesthetically pleasant
- Two-terminal sandwich structure
- TCO | TiO_2 : dye | electrolyte | TCO structure

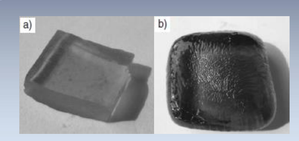


❑ Issues on DSSCs

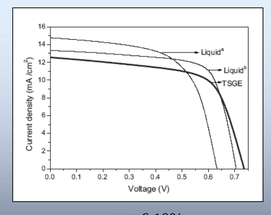
- High photon to electron conversion efficiency
- Large area with high efficiency
- Long-term stability
- Low cost

❑ Recent studies

A Novel Thermosetting Gel Electrolyte for Stable Quasi-Solid-State Dye-Sensitized Solar Cells



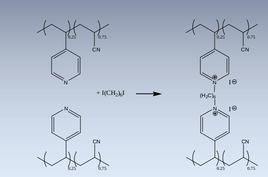
- PAA-PEG hybrid
- Hydrophilic PAA + Amphiphilic PEG
- PAA is superabsorbent with 3D network
- Absorb large amount of liquid
- Micro-sized pore increase with M. W. of PEG



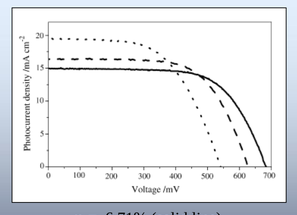
η = 6.10%

J. Wu, *Adv. Mater.* **2007**, 19, 4006-4011

The use of poly(vinylpyridine-co-acrylonitrile) in polymer electrolytes for quasi–solid dye-sensitized solar cells



- Cross-linked P (VPy-co-AN)
- $I(CH_2)_6I$ used as cross-linking agent



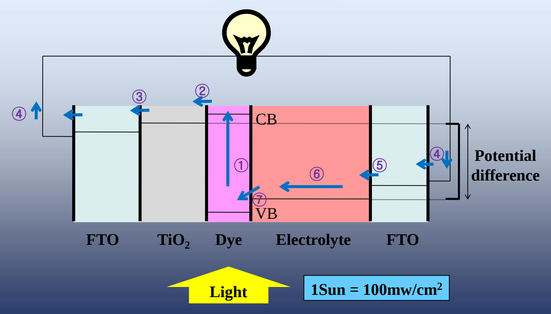
η = 6.71% (solid line)

M. Li, Yuan, Li, *Electrochim. Acta* **2007**, 52, 4858-4863

Principle

❑ Operation mechanism of DSSCs

① Excitation by light(**D + hν → D***)
② Excited electron injected into conduction band (π* orbital) of TiO_2(**D* → D + e⁻**)
③ Electron diffusion to FTO electrode
④ Electron transfer from photo-electrode to counter electrode through external circuit
⑤ At the interface of counter-electrode and electrolyte, Pt catalytic reduction occurred (**I_3^- + 2e⁻ → 3I⁻**)
⑥ I^- ions move to the interface of dye (ion conduction)
⑦ Recombination electron and hole (**3I⁻ → I_3^- + 2e⁻**)



Experimental

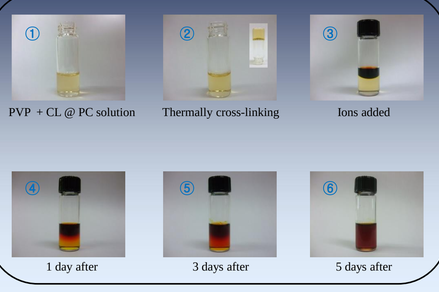
❑ Fabrication process

- Polymer matrix fabrication
  - Poly(4-vinylphenol) : Cross-linking agent : Propylene carbonate
    10 : 5 : 85 (w/w%) ①
  - Heating (140˚C, more than 2 hr)▷ Gelation(②)
- Preparation of polymer gel electrolyte
  - Addition of ions on gel-type Polymer(③) and wait 5 days(④~⑥)

Ion	LiI	I_2	t-BP	GuNCS	MPII
Molar concentration (M)	0.2067	0.1250	2.0831	0.4129	Used as solvent

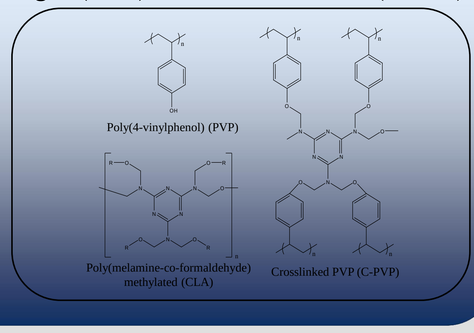
- Fabrication of DSSCs
  - Preparation of TiO_2:Dye film
    - Screen Printing TiO_2, (about 12μm)
    - Sintering 500˚C(by furnace, 30mins)
    - Dying TiO_2 (24hour) (N719)
  - Preparation of counter electrode
    - Spincoating H_2PtCl_6 to cleaned FTO glass
    - Sintering 390˚C (by furnace, 30mins)
  - Sandwich the two electrodes by putting electrolyte and Surlyn (60μm)

Polymer gel electrolyte fabrication process



PVP + CL @ PC solution | Thermally cross-linking | Ions added
1 day after | 3 days after | 5 days after

Chemical structure of PVP, cross-linking agent(CLA) and cross-linked PVP(C-PVP)

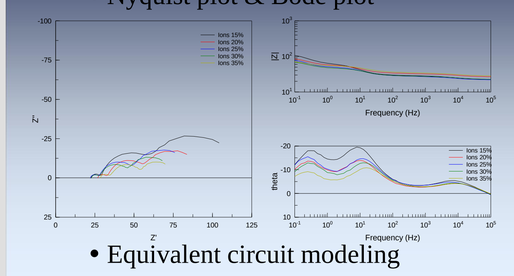


Poly(4-vinylphenol) (PVP)
Poly(melamine-co-formaldehyde) methylated (CLA)
Crosslinked PVP (C-PVP)

Results

❑ Electrochemical analysis

- Nyquist plot & Bode plot



- Equivalent circuit modeling

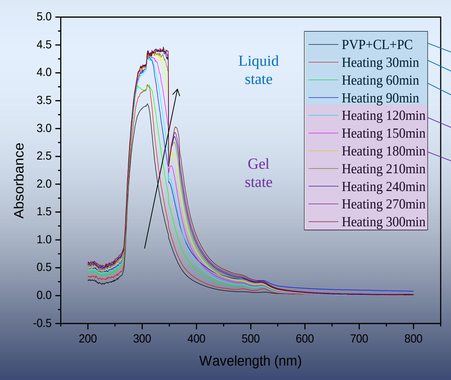
Ion concentration	R1	R2	R3	CPE1T	CPE2T	W1R	W1T
15%	20.48	9.57	27.35	2.17e-4	8.07e-4	54.46	1.756
20%	20.9	13.88	18.76	5.38e-4	8.14e-4	37.22	2.017
25%	19.92	9.35	17.33	5.32e-4	7.81e-4	36.76	2.095
30%	19.75	9.47	14.91	4.34e-4	7.78e-4	28.03	1.78
35%	23.83	12.89	16.07	4.95e-4	7.73e-4	20.71	0.54

- The ion conduction of electrolyte can be modeled using Warburg diffusion element
- There is some tendency that Warburg resistance decreasing as ion concentration increases

Results

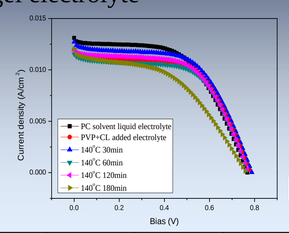
❑ UV-visible spectra

- Heating at 140℃ for *in situ* cross-linking
- Peak shifts to longer wavelength (red shift) with increasing heating time
- Red shift is due to the increase of degree of cross-linking reaction



❑ Photovoltaic properties

- Comparison of DSSC performance based on liquid and gel electrolyte

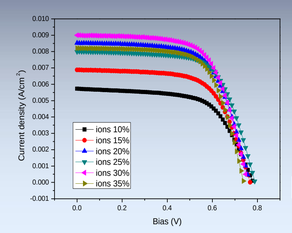


100mW/cm²

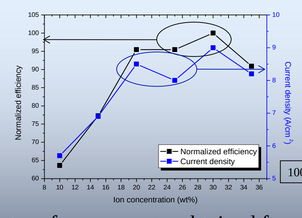
Electrolyte	J_{sc}(mA)	V_{oc}(mV)	F.F.(%)	Efficiency(%)
PC solvent liquid electrolyte	13.1	767.7	54.4	5.5
PVP+CL added electrolyte	12.0	777.8	57.7	5.4
Heating 30 min	12.7	787.9	56.4	5.6
Heating 60 min	11.5	767.7	58.6	5.2
Heating 120 min	**11.9**	**777.8**	**57.6**	**5.3**
Heating 180 min	12.0	757.6	45.3	4.1

- The cross-linking reaction has been carried out at 140 °C
- Best performance (η = 5.3 %) was obtained with DSSC based on gel type electrolyte prepared by heating the solution for 120 min
- DSSC with gel type electrolyte prepared by heating for 180 min showed low η due to low ion conduction.

- DSSC performance *vs* concentration of electrolyte ions



100mW/cm²



100mW/cm²

- The best performance was obtained from DSSC based on gel type electrolyte with 30% ion concentration

Summary

- Cross-linked polymer matrix is fabricated through a thermally induced chemical reaction between PVP and cross-linking agent.
- Cross-linking degree is confirmed by a red shift of absorbance peak of UV-visible spectra, which was measured *in situ* condition.
- The preparation condition and composition of the gel-type polymer electrolyte was optimized:
  - Heating at 140℃ for 2hours.
  - 30wt% electrolyte ion concentration.
- We successfully demonstrated DSSC based on the chemically cross-linked gel type polymer electrolyte and the efficiency was 5.3% .
- In conclusion, chemically cross-linked polymer electrolyte can be suitably applied for long-term stable electrolyte of DSSCs.

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