Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Cite this: DOI: 10.1039/x0xx00000x

Diode-Like Gel Polymer Electrolytes for Full-Cell Lithium Ion Batteries

Yong-Yi Lin, Yen-Ming Chen, Sheng-Shu Hou, Jeng-Shiung Jan, Yuh-Lang Lee, and Hsisheng Teng*

Department of Chemical Engineering, National Cheng Kung University,Tainan 70101, Taiwan

* Corresponding authors: (E-mail): hteng@mail.ncku.edu.tw; (Fax): 886-6-2344496; (Tel): 886-6-2385371

Electronic supplementary information for:

1. **SEM images of GPE's polymeric framework**
2. **Full-range Raman spectra of electrolytes.**
3. **Calculation details for the t_{Li+} values.**
4. **Impedance data of electrolytes at various temperatures.**
5. **Cycling test for the graphite|GPE-PAM-SiTi|$LiFePO_4$ battery**
6. **Comparison of the GPE-PAM-SiTi battery with other GPE-based batteries**

1. SEM images of GPE's polymeric framework

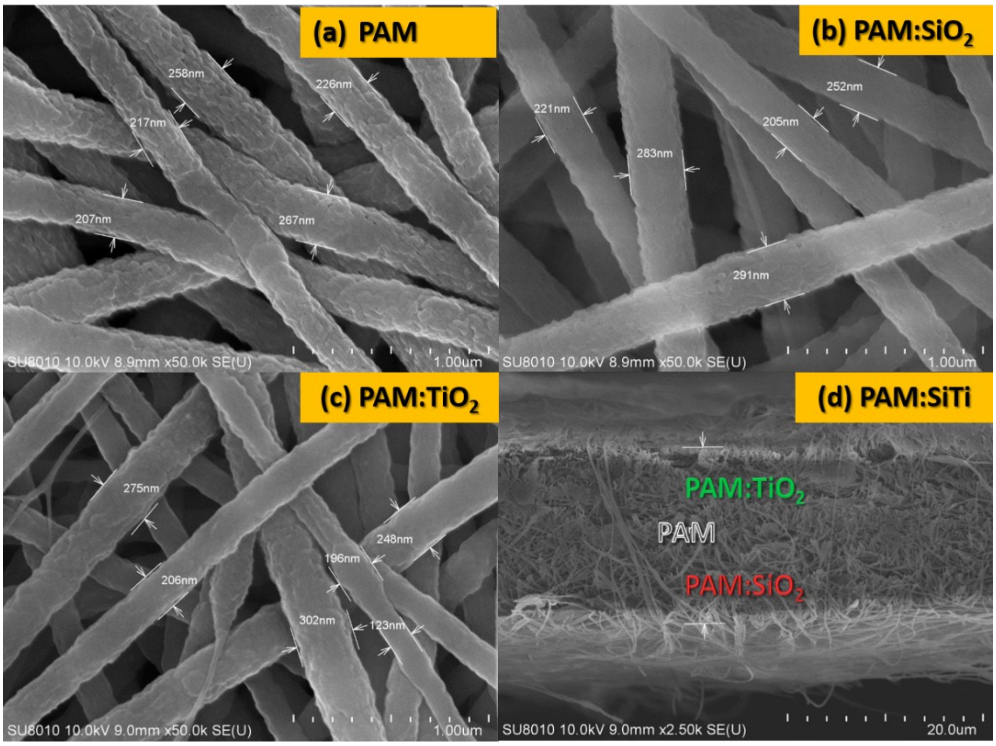

Fig. S1. SEM images of electrospun (a) PAM, (b) PAM:SiO_2, and (c) PAM:TiO_2 membranes consisting of nanofibers and side-view image of the (d) PAM:SiTi membrane comprising PAM:SiO_2, PAM, and PAM:TiO_2 layers connected in series.

2. Full-range Raman spectra of electrolytes

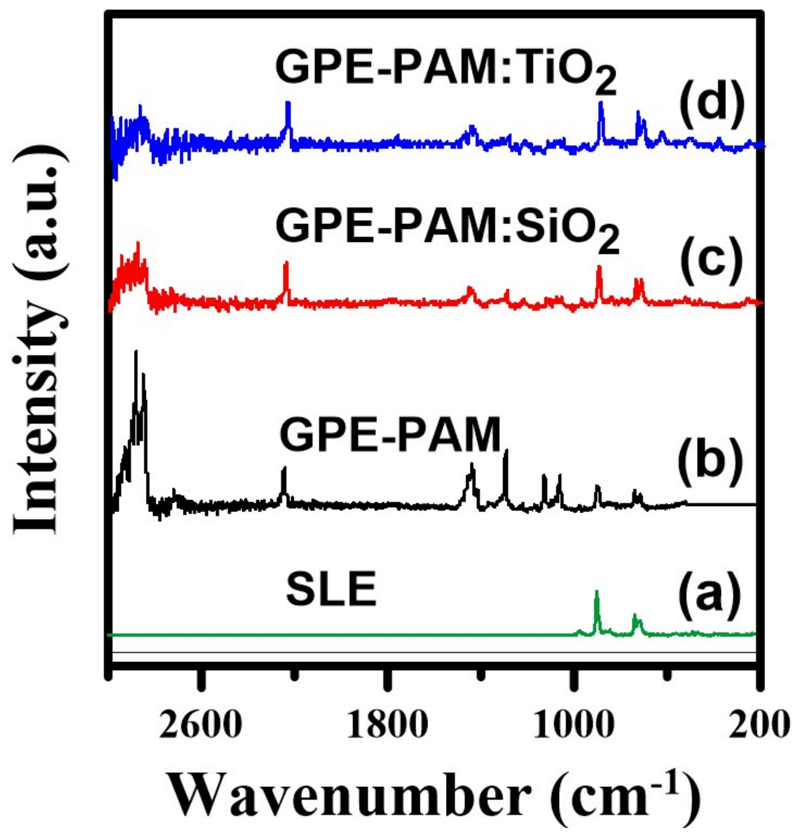

Fig. S2. The full-range Raman spectra of (a) SLE, (b) GPE-PAM, (c) GPE-PAM:SiO_2, and (d) GPE-PAM:TiO_2.

3. Calculation details for the t_{Li+} values

Cells consisting of two Li-metal electrodes sandwiching SLE or GPEs were used to determine the t_{Li+} value according the following equation:[1]

$$t_{Li^+} = \frac{I_{ss}(\Delta V_{DC} - I_0\, R_{int,0})}{I_0(\Delta V_{DC} - I_{ss}\, R_{int,ss})} \quad (2)$$

where I_0 and I_{ss} are the initial and steady-state currents, respectively (Figure S2a), when polarizing the cell to a low DC voltage of 5 mV (V_{DC}). The I_{ss} values were determined when the current variation rate was smaller than 0.1 μA/min. $R_{int,0}$ and $R_{int,ss}$ are the initial and steady-state resistance values associated with charge transfer at the Li-metal interfaces, as determined using AC impedance analysis (Figure S2(b−f)).

Reference

1. J. Evans, C. A. Vincent, P. G. Bruce, *Polymer* **1987**, *28*, 2324.

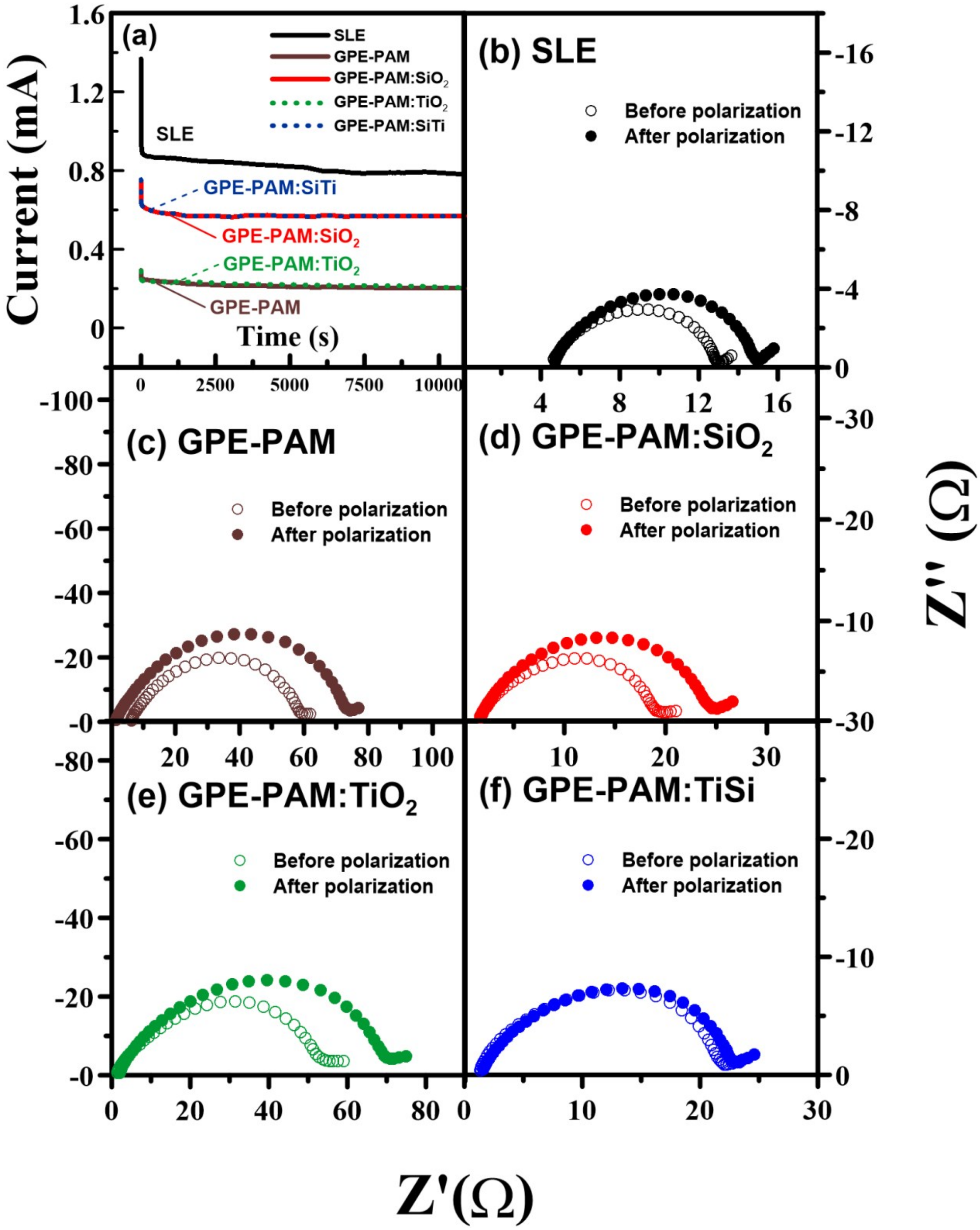

Fig. S3. (a) Current-time curves of Li|electrolyte|Li cells following application of DC voltage (5 mV) to the cell. (b–f) Corresponding Nyquist impedance plots of the cells, (b) SLE, (c) GPE-PAM, (d) GPE-PAM:SiO_2, (e) GPE-PAM:TiO_2, and (f) GPE-PAM:SiTi, which were used to determine the initial and final R_{int} values.

4. Impedance data of electrolytes at various temperatures

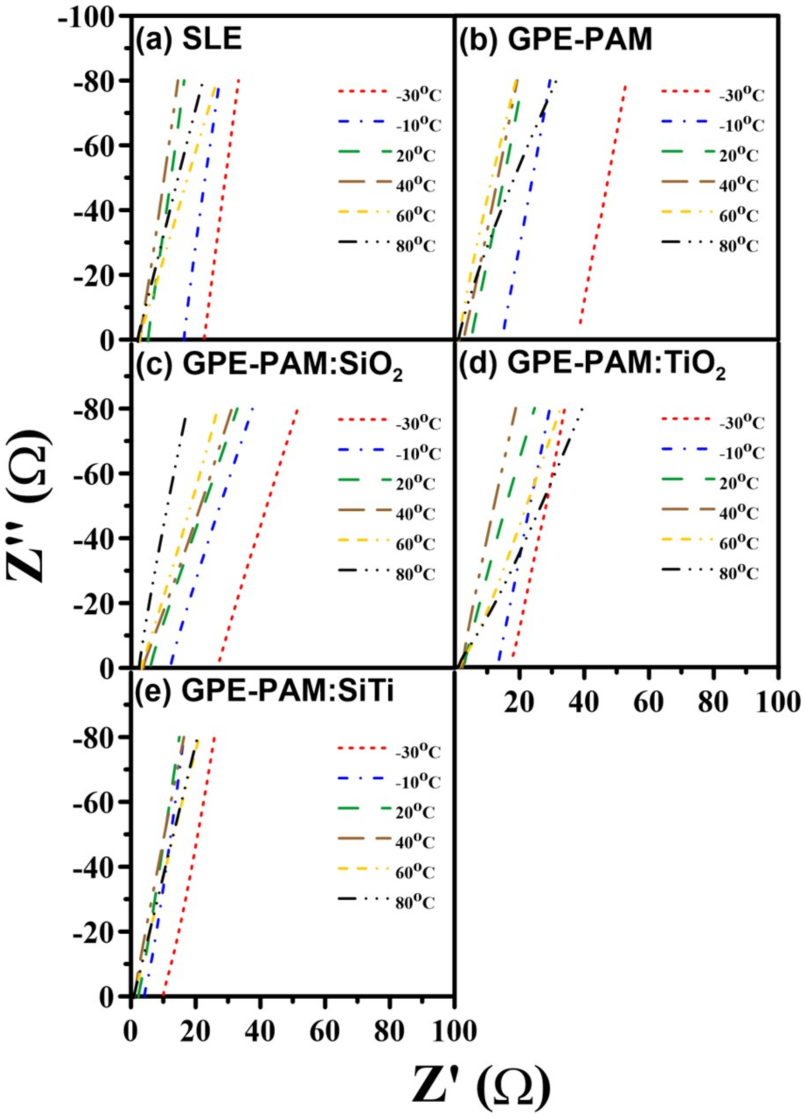

Fig. S4. Nyquist impedance spectra of electrolytes at various temperatures: (a) SLE; (b)GPE-PAM; (c) GPE-PAM:SiO_2; (d) GPE-PAM:TiO_2; (e) GPE-PAM:SiTi. The measurements were conducted by inserting the electrolytes between two stainless-steel electrodes and applying an AC potential amplitude of 5 mV over a frequency range of 0.1 Hz to 100k Hz at temperatures of −30 to 80 °C. The thicknesses of the GPEs and SLE were 50 and 12 μm, respectively.

5. Cycling test for the graphite|GPE-PAM-SiTi|$LiFePO_4$ battery

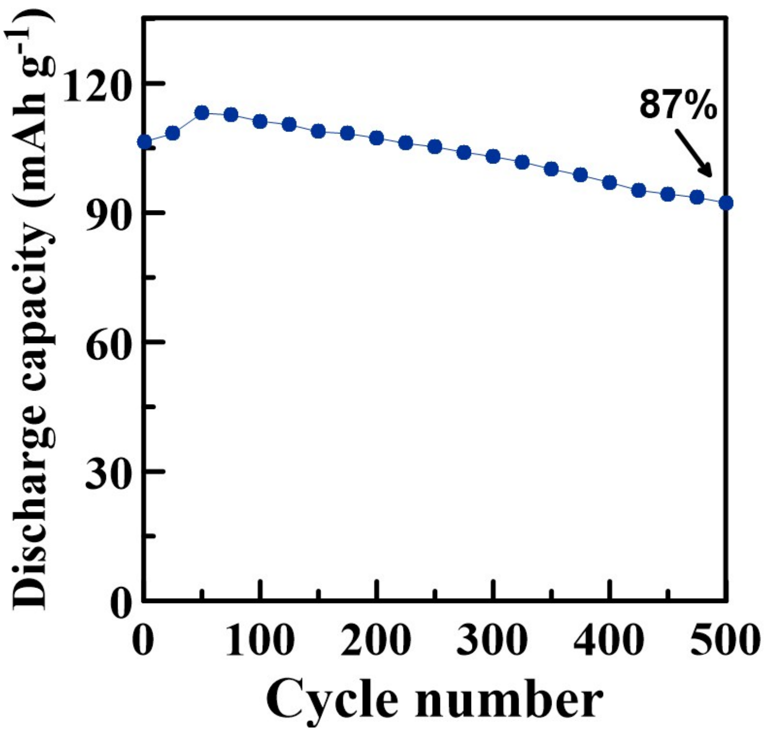

Fig. S5. Discharge capacities of the full-cell graphite|GPE-PAM-SiTi|$LiFePO_4$ battery following 500 cycles of charge–discharge at 5 C-rate over a voltage range of 2.0–3.8 V. The capacity retention at the 500th cycle was presented in the figure.

6. Comparison of the GPE-PAM-SiTi battery with other GPE-based batteries

Table S1. Literature survey: Capacity values and cycle lifespans of graphite|electrolyte|$LiFePO_4$ lithium ion batteries assembled using various electrolytes.

GPE composition: polymer/electrolyte[a]	Electrodes[b]	Capacity (mAh g^{-1})	Cycling retention, cycles/rate	Ref.
P(EO-PO)/ $LiPF_6$-EC-DEC-DMC	G|LFP	125 @ 0.5 C 88 @ 5 C	77%, 450/1 C	1
P(MMA-PEGMA)-PVDF/ $LiPF_6$-EC-DMC-EMC	G|LFP	130 @ 0.1 C 90 @ 2 C	55.6%, 50/1 C	2
PDMS-g-(PPO-PEO)-PVDF/ $LiPF_6$-EC-DMC-EMC	G|LFP	120 @ 1 C	85%, 100/1 C	3
P(OEGMA-BnMA)/ $LiPF_6$-EC-DMC	G|LFP	122 @ 0.1 C 25 @ 5 C	91%, 50/0.5 C	4
PAM:SiTi/ $LiPF_6$-EC-DEC-DMC	G|LFP	137 @ 0.1 C 131 @ 1 C 103 @ 5 C 85.1 @ 7 C	87%, 500/5 C	this work

[a] $LiPF_6$, lithium hexafluorophosphate; EC, ethylene carbonate; DMC, dimethyl carbonate; EMC, ethyl methyl carbonate; DEC, diethyl carbonate; P(EO-PO), poly(ethylene oxide-co-propylene oxide); P(MMA-PEGMA), poly(methyl methacrylate-co-poly(ethylene glycol) methacrylate); PVDF, poly(vinylidene fluoride); PDMS-g-(PPO-PEO), poly(dimethylsiloxane) graft poly(propylene oxide)-co-poly (ethylene oxide); P(OEGMA-BnMA), poly(oligo (ethylene glycol) methyl ether methacrylate-benzyl methacrylate); PAM:SiTi, diode-like membrane comprising poly(acrylonitrile-co-methyl acrylate) doped with TiO_2 and SiO_2 nanoparticles.

[b] G, graphite; LFP, $LiFePO_4$.

1. L. Y. Huang, Y. C. Shih, S. H. Wang, P. L. Kuo and H. S. Teng, *J. Mater. Chem. A,* 2014, **2**, 10492.
2. H. Li, C. E. Lin, J. L. Shi, X. T. Ma, L. P. Zhu and B. K. Zhu, *Electrochim. Acta,* 2014, **115**, 317.
3. H. Li, H. Zhang, Z. Y. Liang, Y. M. Chen, L. P. Zhu and B. K. Zhu, *Electrochim. Acta,* 2014, **116**, 413.
4. P. Isken, M. Winter, S. Passerini and A. L. Balducci, *J. Power Sources,* 2013, **225**, 157.