

Counter anion effects in anion exchange membrane-fabricated non-aqueous vanadium redox flow battery

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Abstract: In order to understand the counter anionic effects in a non-aqueous vanadium redox flow battery (VRFB), we synthesized four types of electrolyte salts (1-ethyltriethamine tetrafluoroborate, [E-TEDA]⁺[BF₄]⁻, 1-ethyltriethamine hexafluorophosphate, [E-TEDA]⁺[PF₆]⁻, 1-butyltriethylamine tetrafluoroborate, [B-TEDA]⁺[BF₄]⁻, and 1-butyltriethylamine hexafluorophosphate [B-TEDA]⁺[PF₆]⁻) by counter anion exchange reaction after the SN₂ reaction. We confirmed the successful synthesis of the electrolyte salts [E-TEDA]⁺[Br]⁻ and [B-TEDA]⁺[Br]⁻ via ¹H-NMR spectroscopy and GC-mass analysis before the counter anion exchange reaction. The electric potential of the vanadium acetylacetonate, V(acac)₃, as an energy storage chemical was shown to be 2.2 V in the acetonitrile solvent with each of the [E-TEDA]⁺[BF₄]⁻, [E-TEDA]⁺[PF₆]⁻, [B-TEDA]⁺[BF₄]⁻, and [B-TEDA]⁺[PF₆]⁻ electrolyte salts. In a non-aqueous VRFB with a commercial Neosepta AFN membrane, the maximum voltages reached 1.0 V and 1.5 V under a fixed current value of 0.1 mA in acetonitrile with the [E-TEDA]⁺[BF₄]⁻ and [E-TEDA]⁺[PF₆]⁻ electrolyte salts, respectively. The maximum voltage was 0.8 V and 1.1 V under a fixed current value of 0.1 mA in acetonitrile with the [B-TEDA]⁺[BF₄]⁻ and [B-TEDA]⁺[PF₆]⁻ electrolyte salts, respectively. From these results, we concluded that in the non-aqueous VRFB more of the [PF₆]⁻ counter anion than the [BF₄]⁻ counter anion was transported onto the commercial Neosepta AFN anion exchange membrane.

Key words: Non-aqueous vanadium redox flow battery, Electrolyte salts, Triethyldiamine, Vanadium acetylacetonate, energy storage chemicals

1. Introduction

Vanadium redox flow battery (VRFB) has received considerable attention in recent years because of its flexibility in design and its facility to regenerate the electrolyte solution. As one of the key components of VRFB, the ion exchange membrane should prevent cross mixing of the positive and negative electrolytes

and allow the transport of ions to complete the circuit during the passage of current.¹⁻³ Therefore, the ideal ion exchange membrane for VRFB should have high ion conductivity, low permeability of vanadium ions, and good stability.^{4,5} Nafion membrane has been investigated for VRFB application owing to its high proton conductivity and good chemical stability.⁶⁻⁸ However, the Nafion membrane is limited in

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commercial application in a VRFB because of its high cost and high permeability of vanadium ions. Although an anion exchange membrane was commonly used as a separator in order to reduce the permeability of vanadium ions in VRFB, little has been reported about the effects of counter anions, which are transported in the anion exchange membrane during the charge and discharge process in a non-aqueous VRFB.

In this study, we synthesized electrolyte salts 1-ethyltriethylamine tetrafluoroborate $[E\text{-TEDA}]^+[\text{BF}_4]^-$, 1-ethyltriethylamine hexafluorophosphate $[E\text{-TEDA}]^+[\text{PF}_6]^-$, 1-butyltriethylamine tetrafluoroborate $[B\text{-TEDA}]^+[\text{BF}_4]^-$, and 1-butyltriethylamine hexafluorophosphate $[B\text{-TEDA}]^+[\text{PF}_6]^-$ by counter anion exchange reaction after the $\text{S}_\text{N}2$ reaction. The electric potential of the vanadium acetylacetonate, $\text{V}(\text{acac})_3$, as an energy storage chemical was determined in acetonitrile electrolyte in the presence of each of the synthesized electrolyte salts. The battery performance was examined in a flow single cell device including commercial Neosepta AFN as an anion exchange membrane in order to determine the efficiency of the counter anion of the organic electrolyte to the anion exchange

membrane.

2. Experimental

2.1. Materials

1,4-Diazabicyclo[2,2,2]octane triethylamine (TEDA), vanadium acetylacetonate ($\text{V}(\text{acac})_3$), poly (vinyl chloride), cyclohexanone, bromoethane, and bromobutane were purchased from Sigma-Aldrich Co. and used without any purification. A commercial anion exchange membrane Neosepta AFN was obtained from Inomeditech Co. (Seoul Korea) and a glassy carbon electrode (GCE, MF-2012) from Bioanalytical Systems, Inc. (USA). A conventional three-electrode system was used comprising a composite-coated glassy carbon (diameter, 3.0 mm) working electrode, a platinum wire counter electrode, and an Ag/AgCl (saturated KCl) reference electrode.

2.2. Synthesis of the organic electrolyte salts

A schematic diagram of synthesis of the organic salts by counter ion exchange reaction after the $\text{S}_\text{N}2$ reaction is shown in Fig. 1. In detail, first $[E\text{-TEDA}]^+[\text{Br}]^-$ was synthesized by the $\text{S}_\text{N}2$ reaction of TEDA

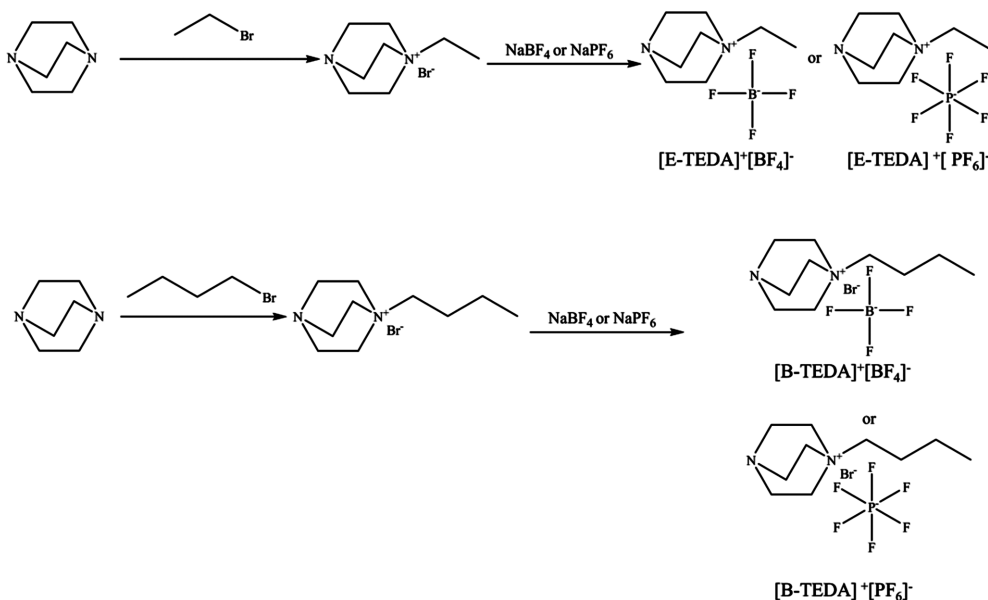


Fig. 1. Schematic synthesis of electrolyte salts, $[E\text{-TEDA}]^+[\text{BF}_4]^-$, $[E\text{-TEDA}]^+[\text{PF}_6]^-$, $[B\text{-TEDA}]^+[\text{BF}_4]^-$, and $[B\text{-TEDA}]^+[\text{PF}_6]^-$ by $\text{S}_\text{N}2$ reaction.

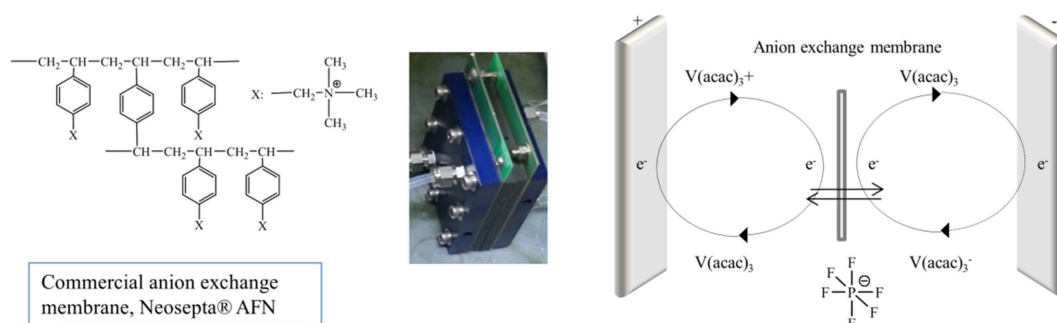


Fig. 2. Structure of the commercial anion exchange membrane, Neosepta® AFN, and the charge-discharge process in non-aqueous vanadium redox flow single cell.

(2.0 g, 17.8 mmol) and bromoethane (1.4 mL, 18.7 mmol) in acetonitrile at room temperature for 24 hours. Also, [B-TEDA]⁺[Br]⁻ was synthesized in a similar way to the above described method. The resulting solutions were washed in ether in order to remove any unreacted reactants and separate the organic electrolyte, and this procedure was repeated three times in order to obtain pure organic electrolytes. Finally, pure [E-TEDA]⁺[Br]⁻ and [B-TEDA]⁺[Br]⁻ were obtained through vacuum evaporation of the solvent.

The [E-TEDA]⁺[BF₄]⁻ and [B-TEDA]⁺[BF₄]⁻ were obtained by counter ion exchange reaction of [E-TEDA]⁺[Br]⁻ and [B-TEDA]⁺[Br]⁻ using NaBF₄ in acetonitrile at 25 °C for 3 days with constant stirring. The [E-TEDA]⁺[PF₆]⁻ and [B-TEDA]⁺[PF₆]⁻ were synthesized by counter ion exchange reaction of [E-TEDA]⁺[Br]⁻ and [B-TEDA]⁺[Br]⁻, respectively, with NaPF₆ in acetonitrile at room temperature for 3 days with constant stirring.

2.3. Characterizations

The synthesized samples were characterized via ¹H-NMR spectroscopy (Inova 600, Varian, Australia) and GC-mass spectrometry (Clarus 600 series, Perkin Elmer, USA).

The charge-discharge cycles were performed using a flow single cell device with two half cells separated by a commercial anion exchange membrane (Neosepta AFN). The charge-discharge experiments were performed in acetonitrile electrolytes with V(acac)₃ of 0.05 M and the synthesized electrolyte salts of 0.05

M using an automatic battery cyclor (WBCS3000, WonATech, Korea). In the anion exchange membrane system, a negative electrolyte such as [PF₆]⁻ was transported onto the anion exchange membrane during the charge-discharge process, while permeability of the positive electrolyte and vanadium cations was prevented by the Donnan effect (Fig. 2).

3. Results and Discussion

The ¹H-NMR spectrum (upper) and GC-mass data (down) of the [E-TEDA]⁺[Br]⁻ and [B-TEDA]⁺[Br]⁻ synthesized by the S_N2 reaction in acetonitrile (Figs. 3 and 4 respectively) confirmed the successful synthesis of these organic electrolyte salts. The proton peaks of [E-TEDA]⁺[Br]⁻ were assigned as shown in the ¹H-NMR spectrum, while the main peak of [E-TEDA]⁺[Br]⁻ appears at m/z 141 (base) and 112 (TEDA) with the other fragment peaks as shown in the GC-mass data (Fig. 3). The proton peaks of [B-TEDA]⁺[Br]⁻ were also assigned as shown in the ¹H-NMR spectrum, while the main peak of [B-TEDA]⁺[Br]⁻ is displayed at m/z 168 (base peak), 161, and 112 (TEDA peak) with the other fragment peaks as shown in the GC-mass data (Fig. 4).

The synthesized [E-TEDA]⁺[Br]⁻ and [B-TEDA]⁺[Br]⁻ could not be used as organic electrolyte salts in non-aqueous VRFB because the [Br]⁻ counter anion acts as a Lewis base and could react with the vanadium cation under the charge-discharge process. Furthermore, the counter anion could react with the VRFB under the charge-discharge process as shown

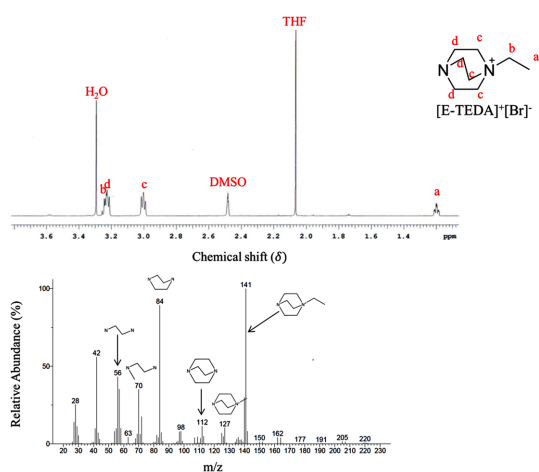
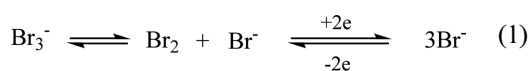


Fig. 3. $^1\text{H-NMR}$ (upper) and GC-mass data (down) of $[\text{E-TEDA}]^+[\text{Br}]^-$.

in following Eq. (1).



Cyclic voltammograms of the $\text{V}(\text{acac})_3$ in acetonitrile in the presence of each of $[\text{E-TEDA}]^+[\text{BF}_4]^-$, $[\text{E-TEDA}]^+[\text{PF}_6]^-$, $[\text{B-TEDA}]^+[\text{BF}_4]^-$, and $[\text{B-TEDA}]^+[\text{PF}_6]^-$ on GCE with 100 mV/s scan rate, respectively.

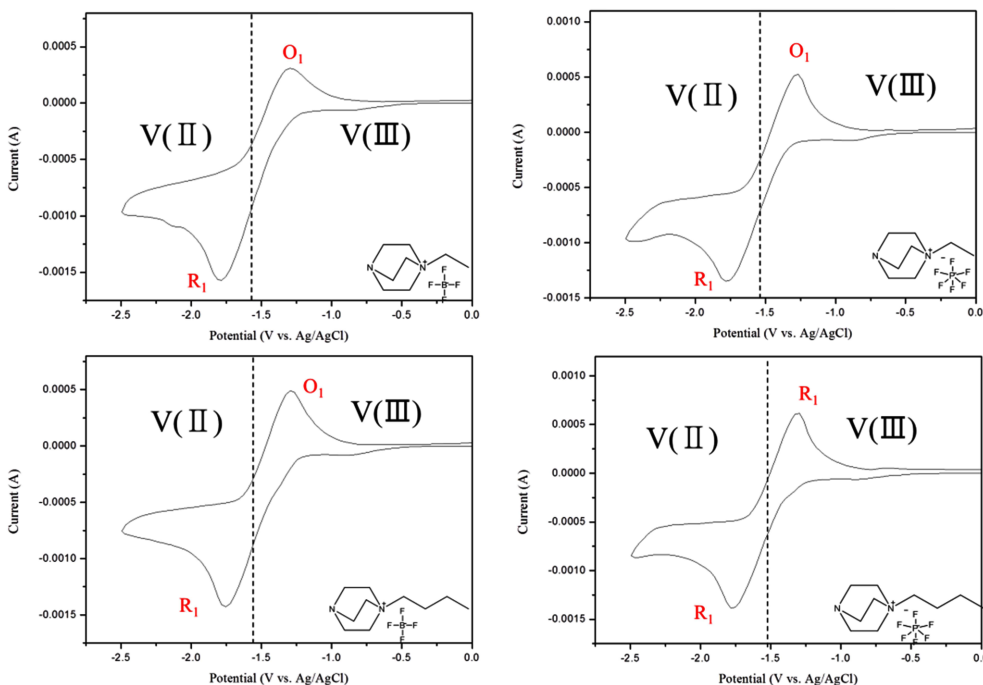


Fig. 5. Cyclic voltammograms of the $\text{V}(\text{acac})_3$ in acetonitrile in the presence of $[\text{E-TEDA}]^+[\text{BF}_4]^-$, $[\text{E-TEDA}]^+[\text{PF}_6]^-$, $[\text{B-TEDA}]^+[\text{BF}_4]^-$, and $[\text{B-TEDA}]^+[\text{PF}_6]^-$ on GCE with 100 mV/s scan rate, respectively.

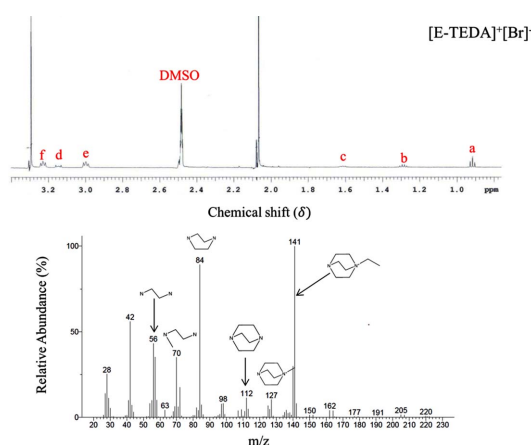


Fig. 4. $^1\text{H-NMR}$ (upper) and GC-mass data (down) of $[\text{E-TEDA}]^+[\text{Br}]^-$.

$\text{TEDA}]^+[\text{PF}_6]^-$, $[\text{B-TEDA}]^+[\text{BF}_4]^-$, and $[\text{B-TEDA}]^+[\text{PF}_6]^-$ on the GCE with a 100 mV/s scan rate are shown in Fig. 5. Redox couples are observed at 2.5~0.0 V for the active species $\text{V}(\text{acac})_3$ in acetonitrile with $[\text{E-TEDA}]^+[\text{BF}_4]^-$, $[\text{E-TEDA}]^+[\text{PF}_6]^-$, $[\text{B-TEDA}]^+[\text{BF}_4]^-$, and $[\text{B-TEDA}]^+[\text{PF}_6]^-$. The current peaks appear in accordance with the following reaction:

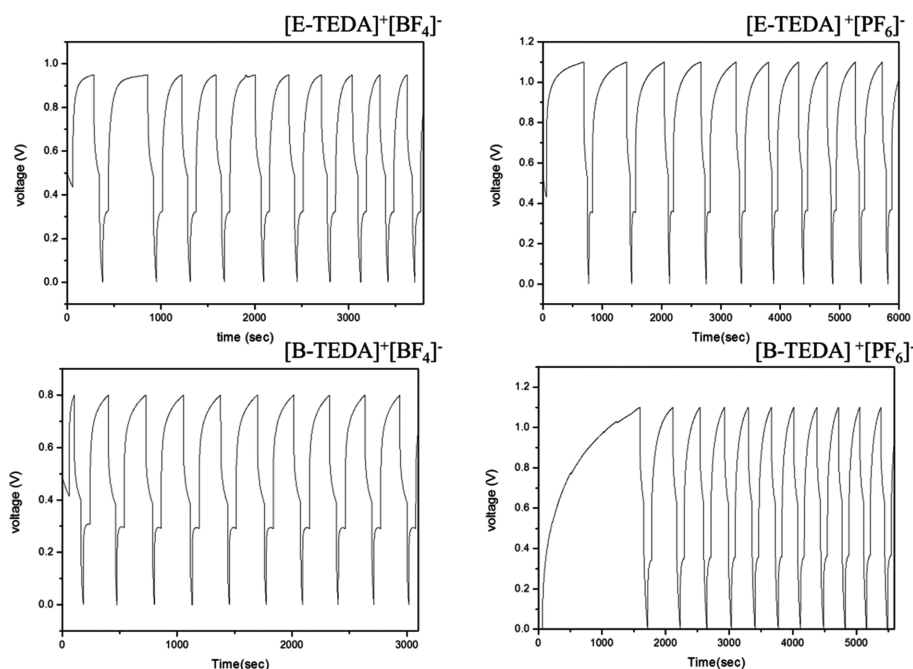
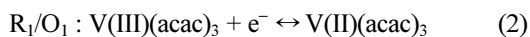


Fig. 6. Vanadium redox battery performance in acetonitrile electrolyte with 0.05M $V(acac)_3$ and 0.05M electrolyte salts. Working condition: $I_c = 0.1$ mA and $I_d = -0.1$ mA; setting voltage = 2.5 V; Neosepta® AFN.



Meanwhile, the weak redox couples of $V(acac)_3$ active species in acetonitrile with each supporting electrolyte are also observed at 0.0 V~1.0 V in accordance with the following reaction:



The electric potentials of the active species $V(acac)_3$ in acetonitrile containing each supporting electrolyte are about 2.2 V for $[E-TEDA]^+[BF_4]^-$, $[E-TEDA]^+[PF_6]^-$, $[B-TEDA]^+[BF_4]^-$, and $[B-TEDA]^+[PF_6]^-$. This means that the maximum energy storage capacity in this $V(acac)_3$ system that could be achieved is 2.2 V for each supporting electrolyte $[E-TEDA]^+[BF_4]^-$, $[E-TEDA]^+[PF_6]^-$, $[B-TEDA]^+[BF_4]^-$, and $[B-TEDA]^+[PF_6]^-$.

The VRFB performance for an acetonitrile electrolyte with 0.05 M $V(acac)_3$ and 0.05 M electrolyte salts is shown in Fig. 6. The experimental condition was prepared as $I_c = 0.1$ mA, $I_d = -0.1$ mA, and setting voltage = 2.5 V. In this experiment, the commercial Neosepta AFN membrane was applied in a flow cell

device. The maximum voltages of the $V(acac)_3$ in acetonitrile electrolyte with $[E-TEDA]^+[BF_4]^-$ and $[B-TEDA]^+[BF_4]^-$ were 0.9 V and 0.8 V, respectively and with $[E-TEDA]^+[PF_6]^-$ and $[B-TEDA]^+[PF_6]^-$ were 1.1 V and 1.1 V, respectively. The maximum voltages of $V(acac)_3$ in the $[PF_6]^-$ counter anion electrolyte are higher than those for the $[BF_4]^-$ counter anion electrolyte. We consider that this is because the $[PF_6]^-$ counter anions possess higher electronegativity than the $[BF_4]^-$ counter anions, which enables more of the $[PF_6]^-$ counter anions to be transmitted onto the anion exchange membrane. Also, we were not able to achieve 2.2 V during the charge-discharge cycles because vanadium ions permeate onto the commercial Neosepta AFN membrane as it swells owing to the presence of the organic solvents.

4. Conclusions

$[E-TEDA]^+[BF_4]^-$, $[E-TEDA]^+[PF_6]^-$, $[B-TEDA]^+[BF_4]^-$, and $[B-TEDA]^+[PF_6]^-$ were synthesized and applied in a nonaqueous $V(acac)_3$ redox flow battery

as supporting electrolytes. Cyclic voltammograms indicate that organic electrolytes with the synthesized [E-TEDA]⁺[BF₄]⁻, [E-TEDA]⁺[PF₆]⁻, [B-TEDA]⁺[BF₄]⁻, and [B-TEDA]⁺[PF₆]⁻ are stable in V(acac)₃ and acetonitrile electrolytes at 2.5~1.0 V. From the cyclic voltammograms, the electric potential of V(acac)₃ in the synthesized electrolyte was shown to be 2.2 V. In the charge-discharge performance, the maximum voltages of the V(acac)₃ were higher with the [PF₆]⁻ counter anion electrolyte than with the [BF₄]⁻ counter anion electrolyte.

Acknowledgements

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References

1. T. Mohammadi and M. Skyllas-Kazacos, *J. Membr. Sci.*, **98**(1-2), 77-87 (1995).
2. S. Maurya, S. H. Shin, K. W. Sung and S. H. Moon, *J. Power Sources*, **255**(1), 325-334 (2014).
3. M. Skyllas-Kazacos, N. A. Milne and G. C. Kazacos, *Mater. Forum*, **32**, 72-77 (2008).
4. X. Li, H. Zhang, Z. Mai, H. Zhang and I. Vankelecom, *Energy Environ. Sci.*, **4**(4), 1147-1160 (2011).
5. X. Luo, Z. Lu, J. Xi, Z. Wu, W. Zhu, L. Chen and X. Qiu, *J. Phys. Chem. B*, 2005, **109**(43), 20310-20314 (2005).
6. C. Sun, J. Chen, H. Zhang, X. Han and Q. Luo, *J. Power Sources*, **195**(3), 890-897 (2010).
7. X. Teng, Y. Zhao, J. Xi, Z. Wu, X. Qiu and L. Chen, *J. Membr. Sci.*, **341**(1-2), 149 -154 (2009).
8. W. Wang, Q. Luo, B. Li, X. Wei, L. Li and Z. Yang, *Adv. Funct. Mater.*, **23**(8), 970-986 (2013).