Supporting Information

Vanadium substituted Keggin-type POMs based electrochromic films showing high performance in Li⁺-based neutral non-aqueous electrolyte

Shi-Ming	Wang*.	Lin	Liu.	Zhi-Yong	Huang	and	Zheng-Bo	Han
Sin wing	wang ,	LIII	Liu,		inuung	unu	Zitcing D0	1 Iuli

The preparation of the $K_{3+n}[PW_{12-n}V_nO_{40}]^{[1]}$:

The synthesis of α -*K*₄[*PW*₁₁*VO*₄₀]: 54g of H₃PW₁₂O₄₀ was dissolved in about 50 mL of water and solid Li₂CO₃ added slowly with vigorous stirring to bring the pH to 4.9. The solution was made up to a total volume of 75 mL, and 100 mL of 0.2 M NaVO₃ was added with stirring. HCI (6 M) was added drop wise to bring the mixture to pH 2 and the solution heated to 60 °C for 10 min before cooling down to room temperature. Additional HCl was added to maintain the pH value equal to 2 and the solution reheated to 60 °C. 20 g of solid KCl was added and the solution maintained at 60 °C for a further 10 min. Cooling to room temperature to obtain yellow precipitate which was collected by filtration.

The synthesis of α -*K*₃[*PW*₁₀*V*₂*O*₄₀]: 30 g Na₈H[PW₉O₃₄] was added to 60 mL of vigorously stirred 20 °C water to produce a white slurry. After 1 min, a solution of 4.2 g of VOSO₄ in 17 mL of water was added dropwise over a period of 10 min and the reaction mixture stirred for an additional 30 min at 20 °C. The temperature of the mixture was increased to 60 °C for 1 h and then Br₂ added until a clear orange solution resulted. Solid KCl (25 g) was stirred in and the mixture heated briefly to 80 °C and then filtered while hot. The cooled filtrate produced 28.3 g of crystalline orange product which recrystallized from 80 °C, pH=2 water gave analytically pure material.

The synthesis of α -K₆[PW₉V₃O₄₀]: 6.1 g NaVO₃ was added to 200mL of 1.0 M sodium acetate/acetic acid buffered at pH=4.8. 40 g Na₈H[PW₉O₃₄] was added and the solution stirred at 25 °C for 48 h. The solution was treated with 30 g of solid KCl and stirred for 30 min. 500 mL methanol was added to produce precipitate which was filtered to give 44 g of tan-orange powder. *The synthesis of Na₈H[PW₉O₃₄]·24H₂O^[2]*: 120g Na₂WO₄·2H₂O is dissolved in 150mL water. 3mL H₃PO₄, and 22 mL concentrated acetic acid are successively added to the solution. Then the white salt Na₈H[PW₉O₃₄]·24H₂O precipitates out.

[1] P. J. Domaille. J. Am. Chem. Soc., 1984, 106, 7677; P. J. Domaille, G. Hervéa, G. Téazéa.
Inorg. Synth. 1990, 27, 96.

[2] R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, M. Fournier. *Inorg. Chem.*, 1977, 16, 2196.



Fig. S1 IR spectra of the TiO₂ substrate (a), α -PW₁₀V₂ (b) and the α -PW₁₀V₂-based composite film(c).



Fig. S2 IR spectra of the TiO_2 substrate (a), α -PW₉V₃ (b) and the α -PW₉V₃-based composite film (c).



Fig. S3 The 100 cycles of CV test of the α -PW₁₁V (a), α -PW₁₀V₂ (b) and α -PW₉V₃ (c) -based EC film in H⁺-based aqueous electrolyte.



Fig. S4 The 100 cycles of CV test of the α -PW₁₁V (a), α -PW₁₀V₂ (b) and α -PW₉V₃ (c) -based EC film in Li⁺-based non-aqueous electrolyte.



Fig. S5 The 2D AFM image of the TiO_2 substrate (a) and the 3D AFM image of the TiO_2 substrate.



Fig. S6 The 3D AFM images of the the α -PW₁₁V-based composite film (a), α -PW₁₀V₂-based composite film (b) and α -PW₉V₃-based composite film (c).



Fig. S7 Visible spectra of the α -PW₁₀V₂-based film (a) and α -PW₉V₃-based film (b) in H⁺-based aqueous electrolyte under different applied potentials.



Fig. S8 Visible spectra of the α -PW₁₀V₂-based film (a) and α -PW₉V₃-based film (b) in Li⁺-based non-aqueous electrolyte under different applied potentials.



Fig. S9 Response time for the α -PW₁₀V₂-based film (a) and α -PW₉V₃-based film (b) in H⁺-based aqueous electrolyte.



Fig. S10 Response time for the α -PW₁₀V₂-based film (a) and α -PW₉V₃-based film (b) in Li⁺-based non-aqueous electrolyte.



Fig. S11 Potential (a), current (b) and transmittance (c) at 650 nm of the α -PW₁₀V₂based EC film during the subsequent double-potential step chronoamperometric experiments of -1.0 V to +1.0 V in H⁺-based aqueous electrolyte.



Fig. S12 Potential (a), current (b) and transmittance (c) at 550 nm of the α -PW₉V₃based EC film during the subsequent double-potential step chronoamperometric experiments of -1.5 V to +1.0 V in H⁺-based aqueous electrolyte.



Fig. S13 Potential (a), current (b) and transmittance (c) at 690 nm of the α -PW₁₀V₂based EC film during the subsequent double-potential step chronoamperometric experiments of -1.8 V to +1.5 V in Li⁺-based non-aqueous electrolyte.



Fig. S14 Potential (a), current (b) and transmittance (c) at 655 nm of the α -PW₁₀V₂based EC film during the subsequent double-potential step chronoamperometric experiments of -1.8 V to +1.5 V in Li⁺-based non-aqueous electrolyte.



Fig. S15 The durability tests of the α -PW₁₁V-based EC film (a), α -PW₁₀V₂-based EC film (b) and α -PW₉V₃-based EC film (c) in Li⁺-based non-aqueous electrolyte.



Fig. S16 The durability tests of the α -PW₁₁V-based EC film (a), α -PW₁₀V₂-based EC film (b) and α -PW₉V₃-based EC film (c) in H⁺-based aqueous electrolyte.