



Cite this: *RSC Adv.*, 2017, 7, 32327

Received 5th April 2017  
 Accepted 20th June 2017

DOI: 10.1039/c7ra03885b

[rsc.li/rsc-advances](http://rsc.li/rsc-advances)

## Y-doped V<sub>2</sub>O<sub>5</sub> with enhanced lithium storage performance

J. H. Yao,<sup>ab</sup> Z. L. Yin,<sup>\*a</sup> Z. G. Zou<sup>c</sup> and Y. W. Li<sup>id</sup><sup>\*b</sup>

Y-doped V<sub>2</sub>O<sub>5</sub> was prepared by the sol–gel method combined with the freeze drying technique followed by annealing in air. The microstructure of the Y-doped V<sub>2</sub>O<sub>5</sub> was analyzed by XRD, SEM, XPS, and first-principles calculations. The electrochemical performance of the Y-doped V<sub>2</sub>O<sub>5</sub> was characterized by CV, EIS, and charge–discharge tests. The results demonstrated that Y doping had great influence on the morphology and crystalline orientation of the prepared V<sub>2</sub>O<sub>5</sub> sample. In particular, Y formed covalent bonds with the adjacent O atoms within the V<sub>2</sub>O<sub>5</sub> layers and decreased the bond orders of the neighboring V–O bonds. Compared with undoped V<sub>2</sub>O<sub>5</sub>, Y-doped V<sub>2</sub>O<sub>5</sub> showed much improved rate capability, higher lithium ion diffusion coefficient, lower electrochemical reaction resistance, and greatly enhanced cycling stability. Y-doped V<sub>2</sub>O<sub>5</sub> could be a promising cathode material for lithium ion batteries.

### 1. Introduction

Lithium-ion batteries (LIBs) have been widely used as power sources for portable electronic devices, and are being developed for high-power applications, such as electric vehicles and hybrid electric vehicles.<sup>1,2</sup> In this context, further improvements in the energy and power densities, safety, and lifetime of LIBs are urgently required. The development of new and improved electrode materials is very crucial for the production of high performance LIBs.<sup>3</sup> There has been much progress in the exploration of different anode materials for LIBs.<sup>4,5</sup> In contrast, the capacity of the cathode is usually far below that of the anode, which limits the development of high power and energy density LIBs.<sup>6,7</sup> Among the potential cathode materials for the next generation LIBs, orthorhombic vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) has been attracting great attention due to its very high theoretical capacity (294 mA h g<sup>−1</sup> when storing two Li<sup>+</sup>), good safety, low cost, and abundant sources.<sup>8–11</sup> However, drawbacks such as poor structural stability, low electronic and ionic conductivity, and slow electrochemical kinetics drastically reduce its cycling stability and rate capability. To overcome these drawbacks, numerous efforts have been carried out. Some groups prepared V<sub>2</sub>O<sub>5</sub> with various nanostructures, such as nanorods,<sup>12,13</sup> nanoribbons,<sup>14,15</sup> nanowires,<sup>16–18</sup> nanosheets,<sup>19–22</sup> porous/hollow spheres,<sup>23–25</sup> and even hierarchical/heterogeneous nanostructures.<sup>26,27</sup> These nanostructured materials showed enhanced electrochemical kinetics, specific

capacity, and rate performance than the pristine V<sub>2</sub>O<sub>5</sub> due to their small size and large surface area, which could greatly increase the contact area between active materials and electrolyte, shorten the diffusion pathways of Li<sup>+</sup>, and relax the mechanical stress associated Li<sup>+</sup> intercalation/deintercalation.<sup>28–30</sup> However, it should be noted that these nanostructured V<sub>2</sub>O<sub>5</sub> still suffered from poor cycling stability because of the intrinsic poor electronic conductivity and/or crystal structural fracture during Li<sup>+</sup> intercalation/deintercalation process. In order to improve the capacity retention of V<sub>2</sub>O<sub>5</sub>, some guest cations, such as Cu<sup>2+</sup>,<sup>31</sup> Mn<sup>2+</sup>,<sup>32</sup> Fe<sup>3+</sup>,<sup>33</sup> Cr<sup>3+</sup>,<sup>34</sup> Al<sup>3+</sup>,<sup>35</sup> and Sn<sup>4+</sup>,<sup>36,37</sup> has been introduced into the material matrix. It has been demonstrated the dopant cations increase the structural stability of V<sub>2</sub>O<sub>5</sub>, resulting in improved electrochemical performance. Rare earth elements, which have been regarded as an ‘industrial vitamin’ are widely applied in modern industries. The chemistry of rare earth differs from transition metals because of the nature of the 4f orbitals, which are ‘buried’ inside the atom and are shielded from the atom’s environment by the 4d and 5p electrons.<sup>38</sup> These unique properties can be exploited to accomplish new types of applications that are not possible with transition and main group metals.<sup>39–41</sup> However, there are few reports about the influence of rare earth element doping on the electrochemical performance of V<sub>2</sub>O<sub>5</sub>. In particular, the action mechanism of dopant cations has not been well understood till now. Herein, we prepared Y-doped V<sub>2</sub>O<sub>5</sub> material by a facile sol–gel method combined with freeze drying technique followed with annealing in air. The effect of Y doping on the microstructure of V<sub>2</sub>O<sub>5</sub> was analyzed by physical characterizations combined with first-principles calculations, and the electrochemical properties of the Y-doped V<sub>2</sub>O<sub>5</sub> were evaluated as potential cathode materials for LIBs.

<sup>a</sup>School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China. E-mail: 3222748031@qq.com

<sup>b</sup>College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, China. E-mail: lywhit@126.com

<sup>c</sup>College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China



## 2. Materials and methods

### 2.1 Synthesis of Y-doped V<sub>2</sub>O<sub>5</sub>

All the chemical reagents were of analytical purity and used without further purification. The synthesis of Y-doped V<sub>2</sub>O<sub>5</sub> follows three main processes. Firstly, V<sub>2</sub>O<sub>5</sub> gel was prepared using the method derived from the one initially developed by Fontenot *et al.*<sup>42</sup> In brief, 0.25 g V<sub>2</sub>O<sub>5</sub> powder was added into 3.85 mL de-ionized (DI) water and 1.15 mL H<sub>2</sub>O<sub>2</sub> (30 wt% in H<sub>2</sub>O) to form a yellow suspension. The above suspension was stirred for 15 min and sonicated for 15 min respectively while kept in water bath at room temperature for reactions to form a transparent red solution. Then 20 mL DI water was added in the red solution and sonicated for about 1 h to form a brownish red V<sub>2</sub>O<sub>5</sub> gel. Secondly, Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added into the V<sub>2</sub>O<sub>5</sub> gel, dispersed and diluted by adding DI water to form a homogenous solution with  $C_{V_2O_5} = 0.03$  M and the  $n(Y) : n(V)$  of 3%. This solution was pre-frozen in a refrigerator for 1 day and then the solvent (water) in the frozen sample was removed using a freeze dryer (FD-1A-50, Boyikang Corp., Beijing, China) under a vacuum at  $-50$  °C for 2 days to get the Y-doped V<sub>2</sub>O<sub>5</sub> precursor. Thirdly, the Y-doped V<sub>2</sub>O<sub>5</sub> precursor was annealed in air at 400 °C for 1 h to form Y-doped V<sub>2</sub>O<sub>5</sub>. For comparison, pure V<sub>2</sub>O<sub>5</sub> was also prepared under the same condition described above but without adding Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O.

### 2.2 Computational method

The geometric and electronic structures of the samples were calculated using plane-wave based density functional theory with a CASTEP program package.<sup>43</sup> The super cell (V<sub>16</sub>O<sub>40</sub>) was used to model pure V<sub>2</sub>O<sub>5</sub> (Fig. 1a) and Y-doped V<sub>2</sub>O<sub>5</sub> (V<sub>16</sub>O<sub>40</sub>Y) was constructed by inserting one Y atom in between two adjacent V<sub>2</sub>O<sub>5</sub> layers (Fig. 1b). The two models are shown in Fig. 1. The exchange–correlation function is PBEsol of the generalized gradient approximation (GGA).<sup>44</sup> The interaction between valence electrons and the ionic core was described by the ultrasoft pseudopotential.<sup>45</sup> A plane-wave cutoff energy of 400 eV and a  $k$ -point mesh of  $1 \times 2 \times 2$  were used for the geometry optimizations. The threshold for self-consistent field iterations is  $5 \times 10^{-7}$  eV per atom. The convergence tolerance parameters of optimized calculation were the energy of  $5 \times$

$10^{-6}$  eV per atom, the maximum force of 0.01 eV Å, the maximum inner stress of 0.02 GPa and the maximum displacement of  $5 \times 10^{-5}$  nm.

### 2.3 Material characterization

The crystal structure of the prepared samples was determined on X'Pert3 diffractometer (PANalytical, Netherlands) with a Cu-K $\alpha$  radiation source ( $\lambda = 1.54056$  Å). The morphology of the prepared samples was characterized on a field-emission scanning electron microscopy (FE-SEM) (Hitachi, SU-5000). The content of Y and the valent state of V in the prepared samples were analyzed by XPS spectrometer (ESCALAB 250Xi) using monochromic AlK $\alpha$  excitation. The pressure in the analytical chamber during spectral acquisition was  $10 \times 10^{-10}$  mbar. To evaluate the exact amount of Y actually present in the synthesized material, inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer Optima 2000 DV) was also carried out in addition to the XPS analysis.

### 2.4 Electrochemical measurements

The electrochemical performances of the samples were tested using CR 2016 coin-type cell with metallic lithium as the anode and polypropylene (PP) film as the separator. The cathodes were fabricated by mixing Y-doped V<sub>2</sub>O<sub>5</sub>, super P carbon black, and poly(vinylidene fluoride) (PVDF) with a weight ratio of 70 : 20 : 10 in *n*-methyl-2-pyrrolidone (NMP) solvent. The resulting slurry was then uniformly spread on an aluminium foil current collector. The cathodes were dried at 80 °C for 12 h in an oven and then punched into small disks with a diameter of 15 mm. The thickness of the electrode was about 15  $\mu$ m and the mass loading of the active material was about 1.0 mg cm<sup>-2</sup>. The electrolyte solution was made of 1 M LiPF<sub>6</sub> in EC/DMC/DEC (1 : 1 : 1 by weight). The cells were galvanostatically charged and discharged between 2.0 V and 4.0 V (*vs.* Li/Li<sup>+</sup>) using LAND-CT2001A battery tester at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (CHI 760). The CV test was performed between 2.0 and 4.0 V at scan rates ranging from 0.1 to 0.5 mV s<sup>-1</sup>. The EIS was measured in the frequency range from 0.01 Hz to 100 kHz at the open circuit voltage (OCV) after given discharge/charge cycles with 5 mV voltage amplitude.

## 3. Results and discussion

### 3.1 Structure characterizations

Fig. 2 presents the XRD patterns of the pure V<sub>2</sub>O<sub>5</sub> and Y-doped V<sub>2</sub>O<sub>5</sub> samples. Both pure V<sub>2</sub>O<sub>5</sub> and Y-doped V<sub>2</sub>O<sub>5</sub> samples show a single orthorhombic V<sub>2</sub>O<sub>5</sub> phase (JCPDS card no. 41-1426) without detectable secondary phase. The lattice constants of the samples were calculated based on the *Pmnm* space group, which were  $a = 11.493$  Å,  $b = 3.562$  Å,  $c = 4.369$  Å for pure V<sub>2</sub>O<sub>5</sub> and  $a = 11.515$  Å,  $b = 3.566$  Å,  $c = 4.373$  Å for Y-doped V<sub>2</sub>O<sub>5</sub>. The results suggest that the Y doping causes slight lattice expansions in V<sub>2</sub>O<sub>5</sub>. From this changes of lattice constants, it can be deduced that the doped Y is likely to locate between the VO<sub>5</sub> slabs and

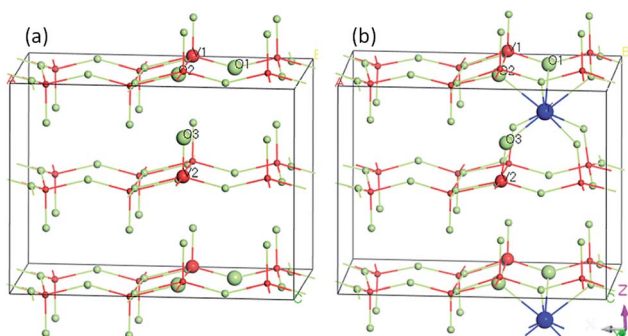


Fig. 1 Computational models of (a) pure V<sub>2</sub>O<sub>5</sub> supercell (V<sub>16</sub>O<sub>40</sub>) and (b) Y-doped V<sub>2</sub>O<sub>5</sub> (V<sub>16</sub>O<sub>40</sub>Y).



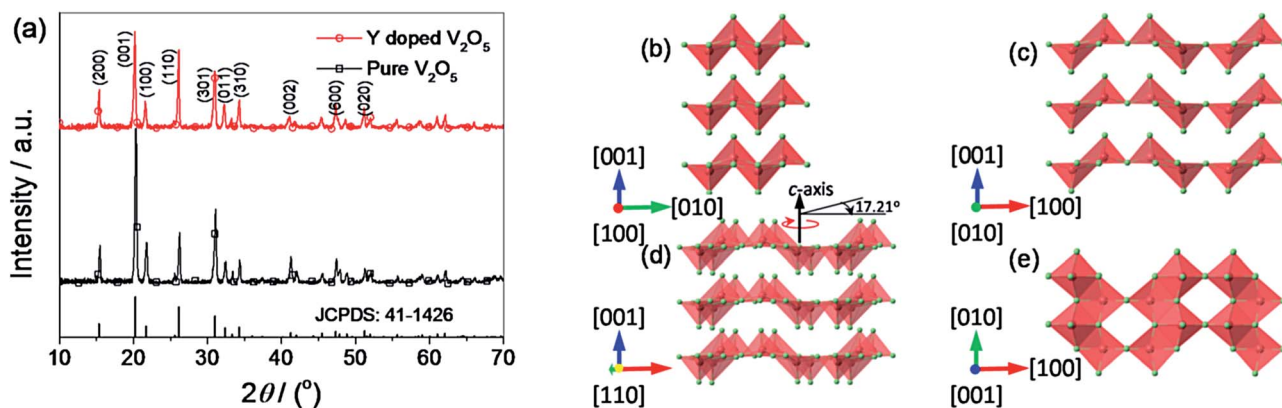


Fig. 2 (a) XRD patterns of the pure  $V_2O_5$  and Y-doped  $V_2O_5$ . The vertical lines on the x-axis correspond to the standard XRD reflections of orthorhombic  $V_2O_5$ . (b–e) The refined structural model of the orthorhombic  $V_2O_5$  viewed along the [100] (b), [010] (c), [110] (d), and [001] (e) directions. The V atoms and O atoms are colored by light red and light green, respectively.

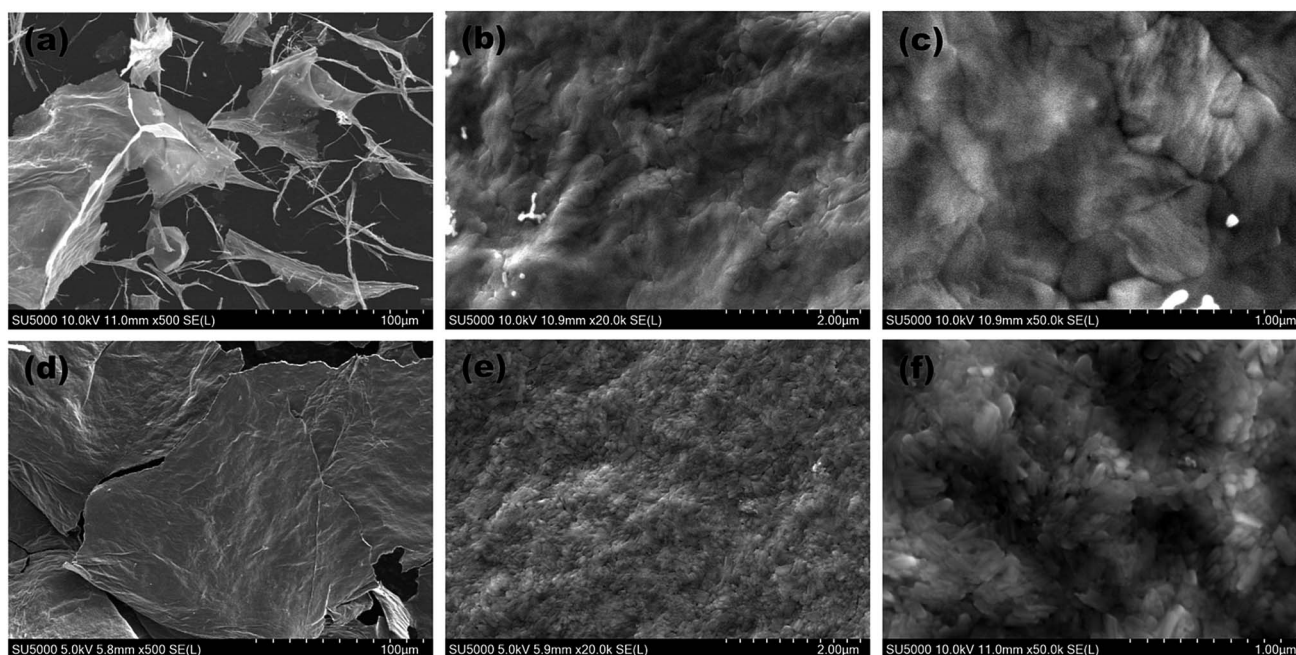


Fig. 3 SEM images of the (a–c) pure  $V_2O_5$  and (d–f) Y-doped  $V_2O_5$ .

forming the  $[YO_6]$  octahedral with oxygen atoms in the  $V_2O_5$  structure.<sup>46</sup> By careful observation, it can be found that there is obvious difference of the relative intensities of (001) and (110) diffraction peaks for the two samples. For Y-doped  $V_2O_5$ , the intensity ratio between (110) and (001) diffractions is 0.81, which is significantly larger than that (0.31) of pure  $V_2O_5$ . This indicates that the Y-doped  $V_2O_5$  exposed more facets than the pure  $V_2O_5$ . As illustrated in Fig. 2c and d, the (010) crystal plane that has the two-dimensional diffusion path is presented when the (110) crystal plane is turned  $17.21^\circ$  along the  $c$  axis. Clearly, this unique crystal orientation of the Y-doped  $V_2O_5$  can facilitate lithium ion intercalation and deintercalation.

Fig. 3 gives the SEM images of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  samples. There is significant difference between the

morphologies of the two samples. The pure  $V_2O_5$  shows mixed sheet-like and fibrous morphologies. The lateral size of the sheets in pure  $V_2O_5$  ranges from several to several ten microns. Moreover, these sheets have a rather smooth surface. The diameter of the fibers in pure  $V_2O_5$  is a few tens to a few hundreds of nanometers. In contrast, the Y-doped  $V_2O_5$  presents only sheet-like morphology and the lateral size (few hundreds of microns) of these  $V_2O_5$  sheets are much larger than that of the pure  $V_2O_5$ . In addition, the  $V_2O_5$  sheets consist of interconnected nanoparticles and show a rather coarse and porous surface. This indicates that Y dopant could greatly modify the morphology of  $V_2O_5$ . For the Y-doped  $V_2O_5$ , this nano-sized building blocks (nanoparticles) and porous 2D sheet-like structure are anticipated to offer fast transport of Li-



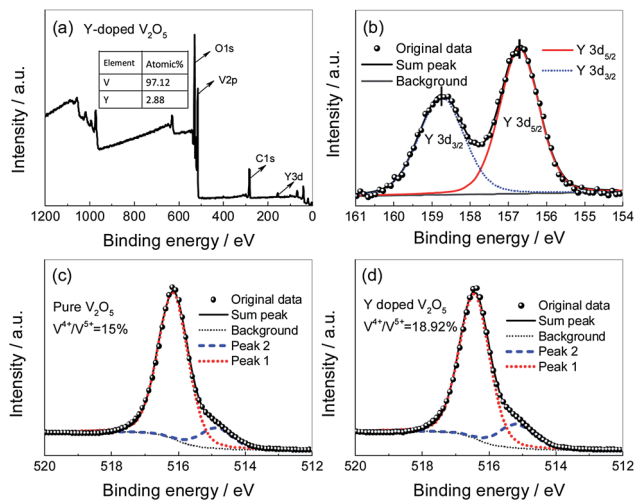


Fig. 4 (a) XPS survey spectrum of the Y-doped  $V_2O_5$ ; (b) high-resolution spectra for Y 3d performed on the Y-doped  $V_2O_5$ ; (c) high-resolution spectra for V  $2p_{3/2}$  performed on the pure  $V_2O_5$ ; (d) high-resolution spectra for V  $2p_{3/2}$  performed on the Y-doped  $V_2O_5$ .

ions and electrons, large material-electrolyte contact area, and easy penetration and diffusion of electrolyte, which are crucial for the improvement of rate performance of electrode materials. Moreover, the pores could also effectively relax the mechanical strain generated upon the lithium ion intercalation/deintercalation cycles.

To investigate the oxidation state of vanadium, XPS measurements were carried out on the pure  $V_2O_5$  and Y-doped  $V_2O_5$ . Fig. 4a shows the XPS survey spectrum of Y-doped  $V_2O_5$ . The line belongs to Y is observed in the spectra and the calculated atomic ratio of  $n(Y) : n(V)$  is of 2.96%. Furthermore, ICP-AES measurement revealed that the  $n(Y) : n(V)$  in the Y-doped  $V_2O_5$  sample is 2.99%. The results from XPS and ICP-AES measurements were consistent and almost equal to the theoretical value of 3%, suggesting that Y was successfully doped in  $V_2O_5$ . Fig. 4b depicts the XPS spectra take from the Y 3d regions. Two intense peaks at 156.7 and 158.8 eV correspond to the binding energy of Y  $3d_{5/2}$  and Y  $3d_{3/2}$ , respectively. The energy difference between Y  $3d_{5/2}$  and Y  $3d_{3/2}$  is 2.1 eV, which is identical to the standard energy difference value for  $Y_2O_3$ ,<sup>47</sup> indicating that the oxidation state of Y ions in Y-doped  $V_2O_5$  is mainly trivalent. Fig. 4c and d present the V  $2p_{3/2}$  core peak spectra of the pure  $V_2O_5$  and Y-doped  $V_2O_5$ , respectively. Both of them composes of two components located at 516.4 eV and 515.2 eV, which can be associated with two formal oxidation degree,  $V^{5+}$  and  $V^{4+}$ , respectively. The calculated molar ratios of  $V^{4+}/(V^{4+} + V^{5+})$  in the pure  $V_2O_5$  and Y-doped  $V_2O_5$  are 15% and 19%, respectively. These increased low valence state  $V^{4+}$  in the Y-doped  $V_2O_5$  are necessary to balance the net charge in the crystal structure of  $V_2O_5$  matrix due to the accommodation of  $Y^{3+}$  ions. The low valence state  $V^{4+}$  could enhance the conductivity of  $V_2O_5$  and accordingly facilitate the  $Li^+$  intercalation/deintercalation process in  $V_2O_5$ .<sup>48</sup>

To further understand the effect of Y doping on the geometric and electronic structures of  $V_2O_5$ , first-principles

calculations were performed on both the pure  $V_2O_5$  and Y-doped  $V_2O_5$ . Table 1 presents the selected bond orders and bond lengths of the two model systems. For pure  $V_2O_5$ , the calculated V–O bond lengths are in very good agreement with the available experimental values.<sup>49</sup> After Y doping, the length of these V–O bonds (V1–O1, V1–O2, V1–O3) adjacent to Y atom was elongated obviously and their corresponding bond orders decrease, suggesting the covalent character of these V–O bonds were weakened.<sup>50</sup> Moreover, the Y dopant shows noticeable interaction with the adjacent O atoms in the  $VO_5$  slabs. The bond orders of the Y–O1 and Y–O2 are 0.20 and 0.18, respectively; the bond order of the Y–O3 is up to 0.33, implying that these Y–O bonds have a covalent character. Fig. 5 presents the isosurface of the electron density difference of the pure  $V_2O_5$  and Y-doped  $V_2O_5$ . In this plot a loss of electrons is indicated in yellow, while electron enrichment is indicated in green. As shown in Fig. 5, the bonding O atoms are surrounded by enriched electrons, while the corresponding V atoms are surrounded by fewer electrons. Notably, there is an obvious redistribution of electrons near the doped Y atoms. The Y atom loses

Table 1 The bond lengths and corresponding bond orders of selected V–O and Y–O bonds for the pure  $V_2O_5$  and Y-doped  $V_2O_5$  calculated by first-principles calculations

System	Selected bond	Bond order	Length/Å
Pure $V_2O_5$	V1–O1	0.46	1.776 1.780 <sup>a</sup>
	V1–O2	0.34	1.871 1.881 <sup>a</sup>
	V2–O3	0.81	1.588 1.581 <sup>a</sup>
Y-doped $V_2O_5$	V1–O1	0.39	1.834
	V1–O2	0.30	1.936
	V2–O3	0.70	1.641
	Y–O1	0.20	2.436
	Y–O2	0.18	2.520
	Y–O3	0.33	2.420

<sup>a</sup> Experimental values from ref. 49.

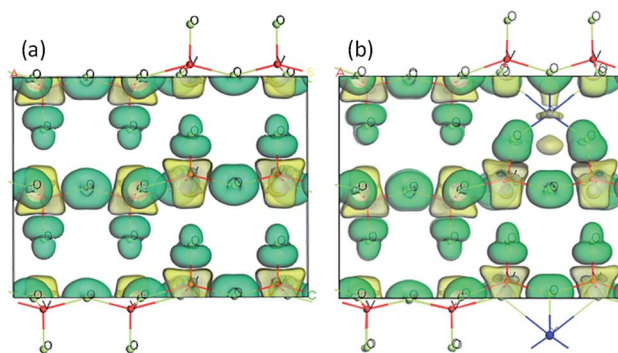


Fig. 5 Electronic density difference isosurfaces for the (a) pure  $V_2O_5$  and (b) Y-doped  $V_2O_5$ . The green region shows the electron accumulation, while the yellow region shows the electron loss. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



electrons and the adjacent O atoms gain electrons. The interaction between Y atom and O atoms is also supported by the distortion of the V–O bond near Y atoms, where the four apical vanadyl oxygen atoms (O3 as labeled in Fig. 1) move closer to the Y atoms.

It is known that the  $\text{Li}_x\text{V}_2\text{O}_5$  will undergo various phase transitions ( $\alpha$ ,  $\varepsilon$ ,  $\delta$ , and  $\gamma$ ) depending on the degree of lithium ion intercalation.<sup>51</sup> In particular, when the lithium intercalation increases up to the range of  $1 < x < 2$ , a structural modification to  $\gamma$ -phase  $\text{Li}_x\text{V}_2\text{O}_5$  occurs, in which the layer puckering becomes more pronounced than in  $\delta$ -phase  $\text{Li}_x\text{V}_2\text{O}_5$  and the  $\text{VO}_5$  pyramids alternate up and down individually, easily resulting collapse of the layer structure and poor cycling stability of  $\text{V}_2\text{O}_5$ . Based on the above theoretical calculation results, it can be deduced that the Y dopant could have two favorable impacts for improving the cycling stability of  $\text{V}_2\text{O}_5$ . First, the chemical interaction between Y atom and the adjacent O atoms in the  $\text{VO}_5$  slabs could stabilize the layer structure of  $\text{V}_2\text{O}_5$  phase during electrochemical interaction of  $\text{Li}^+$ , allowing better structure stability during electrochemical cycling. Second, since the V–O bonds adjacent to Y atom were weakened, these local

structural defects caused by Y dopant may serve as possible nucleation centers for phase transformation during  $\text{Li}^+$  intercalation/deintercalation process, which could also enhance the cycling performance of  $\text{V}_2\text{O}_5$ .

### 3.2 Electrochemical studies

Fig. 6a and b show the cyclic voltammetry (CV) profiles of the first four cycles at a scan rate of  $0.1 \text{ mV s}^{-1}$  for the pure  $\text{V}_2\text{O}_5$  and Y-doped  $\text{V}_2\text{O}_5$  electrodes, respectively. For the pure  $\text{V}_2\text{O}_5$ , three reduction peaks at 3.35 V, 3.10 V, and 2.20 V are observed, which correspond to the  $\alpha/\varepsilon$ ,  $\varepsilon/\delta$ , and  $\delta/\gamma$  phase transitions, respectively.<sup>21,52</sup> However, after this first intercalation process, the electrochemical behavior of the pure  $\text{V}_2\text{O}_5$  is not completely reversible as indicated by the emergence of new redox systems. For example, two additional weak reduction peaks (at 2.35 V and 2.42 V) appear in the low potential region and a new redox couples (3.58/3.64 V) appear in the high potential region. This suggests that the pure  $\text{V}_2\text{O}_5$  undergoes a permanent structural change during the first cycle as reported previously.<sup>21,34,53–56</sup> In contrast, the Y-doped  $\text{V}_2\text{O}_5$  exhibited three well reversible cathodic/anodic redox couples (3.38/3.46 V, 3.16/3.27 V, and

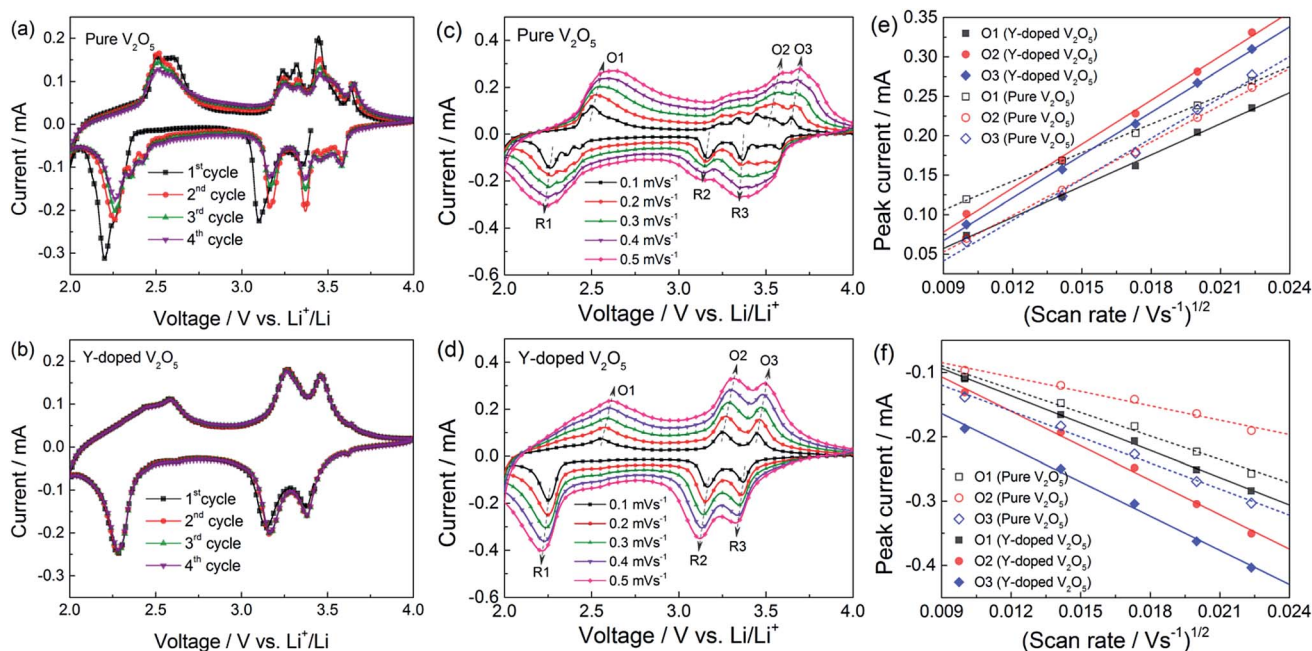


Fig. 6 (a, b) Cyclic voltammetry (CV) profiles of the pure  $\text{V}_2\text{O}_5$  and Y-doped  $\text{V}_2\text{O}_5$  electrodes as a scan rate of  $0.1 \text{ mV s}^{-1}$ . (c, d) CV profiles of the pure  $\text{V}_2\text{O}_5$  and Y-doped  $\text{V}_2\text{O}_5$  electrodes at various scan rates. (e, f) Relationship of the peak current ( $i_p$ ) and the square root of scan rate ( $v^{1/2}$ ) for the pure  $\text{V}_2\text{O}_5$  and Y-doped  $\text{V}_2\text{O}_5$  electrodes. Symbols and lines represent the experimental data and fitted linear lines, respectively.

Table 2 Comparison of the  $\text{Li}^+$  diffusion coefficients ( $D_{\text{Li}}$ ) in the pure  $\text{V}_2\text{O}_5$  and Y-doped  $\text{V}_2\text{O}_5$  electrodes

System	$\text{Li}^+$ diffusion coefficients, $D_{\text{Li}} \times 10^{-12}/\text{cm}^2 \text{ s}^{-1}$					
	Peak O1	Peak O2	Peak O3	Peak R1	Peak R2	Peak R3
Y-doped $\text{V}_2\text{O}_5$	2.227	4.430	4.190	2.567	4.086	4.025
Pure $\text{V}_2\text{O}_5$	1.188	3.082	3.827	1.889	0.713	2.326



2.28/2.59 V) in the whole scanning process as shown in Fig. 6b, implying that the irreversible phase transitions of  $V_2O_5$  are greatly depressed by Y doping. Similar results have also been observed for the Al doped  $V_2O_5$  (ref. 57) and Cr doped  $V_2O_5$ .<sup>34,55,58</sup> Due to the less number of phase transition during the redox process, this Y-doped  $V_2O_5$  is expected to show better cycling performance than the pure  $V_2O_5$ . Moreover, the CV profiles of Y-doped  $V_2O_5$  show good repeatability with cycling, implying that the material has good electrochemical and structural reversibility. To understand the kinetics of  $Li^+$  diffusion in the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes, CV measurements were performed at various scan rates ranging from 0.1 to 0.5  $mV s^{-1}$  and the results are presented in Fig. 6c and d. The oxidation peaks are labeled as O1 to O3, while the reduction peaks as R1 to R3. The good linear relationship (Fig. 6e and f, all the correlation coefficients of linear fit are higher than 0.99) between the peak current ( $i_p$ ) and the square root of the scan rate ( $v^{1/2}$ ) indicates a diffusion-controlled process. In this case, the apparent  $Li^+$  diffusion coefficient ( $D_{Li}$ ) can be evaluated based on the Randles-Sevcik equation:<sup>33,36</sup>

$$i_p = (2.06 \times 10^5) n^{3/2} A D_{Li}^{1/2} C_{Li} v^{1/2} \quad (1)$$

where  $i_p$  is the peak current (A),  $n$  is number of electron involved in the redox process,  $A$  is the electrode area ( $cm^2$ ),  $C_{Li}$  is the concentration of  $Li^+$  in the cathode ( $mol cm^{-3}$ ), and  $v$  is the scan rate ( $V s^{-1}$ ). Table 2 summarized the calculated  $D_{Li}$  values for the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes. Obviously, all the  $D_{Li}$  values of Y-doped  $V_2O_5$  are larger than those of pure  $V_2O_5$ . Similar results were also observed in Sn-doped  $V_2O_5$  and Cu-doped  $V_2O_5$ .<sup>31,36</sup> The larger  $Li^+$  diffusion coefficient of the Y-doped  $V_2O_5$  can be attributed to the unique (110) crystal

orientation, which could provide two-dimensional diffusion paths for  $Li^+$  intercalation as illustrated in Fig. 2d.

Fig. 7a gives the cycling response of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes at a current density of  $200 mA g^{-1}$ . Obviously, the Y-doped  $V_2O_5$  electrode exhibits much better cycling stability than the pure  $V_2O_5$  electrode. In the case of the pure  $V_2O_5$  electrode, the discharge capacity reaches a maximum of  $251 mA h g^{-1}$  at the 2<sup>nd</sup> cycle, which is  $31 mA h g^{-1}$  higher than that ( $220 mA h g^{-1}$ ) of the Y-doped  $V_2O_5$  electrode; but with the increase in cycle number, the discharge capacity of the pure  $V_2O_5$  electrode declines rapidly and at 100<sup>th</sup> cycle the discharge capacity decreases to  $128 mA h g^{-1}$ . This change of discharge capacity is in accordance with the CV results (Fig. 6a). Compared to the 2<sup>nd</sup> cycle, the capacity retention of the pure  $V_2O_5$  electrode at 100<sup>th</sup> cycle is only 51.0%. While for the Y-doped  $V_2O_5$  electrode, the discharge capacity reaches a maximum of 224 at the 10<sup>th</sup> cycle and then decreases very slowly with the increase in cycle number; at 100<sup>th</sup> cycle, the Y-doped  $V_2O_5$  electrode can still deliver a specific discharge capacity of  $203 mA h g^{-1}$ , which is  $75 mA h g^{-1}$  higher than that ( $128 mA h g^{-1}$ ) of the pure  $V_2O_5$  electrode. Compared to the maximum capacity in 10<sup>th</sup> cycle, the capacity retention of the Y-doped  $V_2O_5$  electrode in 100<sup>th</sup> cycle is 90.6%. The capacity retention capability of this Y-doped  $V_2O_5$  is superior to those of the previously reported Cu-doped  $V_2O_5$ , Fe-doped  $V_2O_5$ , Cr-doped  $V_2O_5$ , Al-doped  $V_2O_5$ , and Sn-doped  $V_2O_5$  as summarized in Table 3. Fig. 7b and c show the corresponding discharge/charge voltage profiles of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes at different cycles. Both electrodes show a typical multi-stage discharge/charge profile, which agrees well with the redox peaks shown in the CV curves (Fig. 6a and b). With the cycle number increasing from 2 to 100, the pure  $V_2O_5$  electrode shows a significant increase

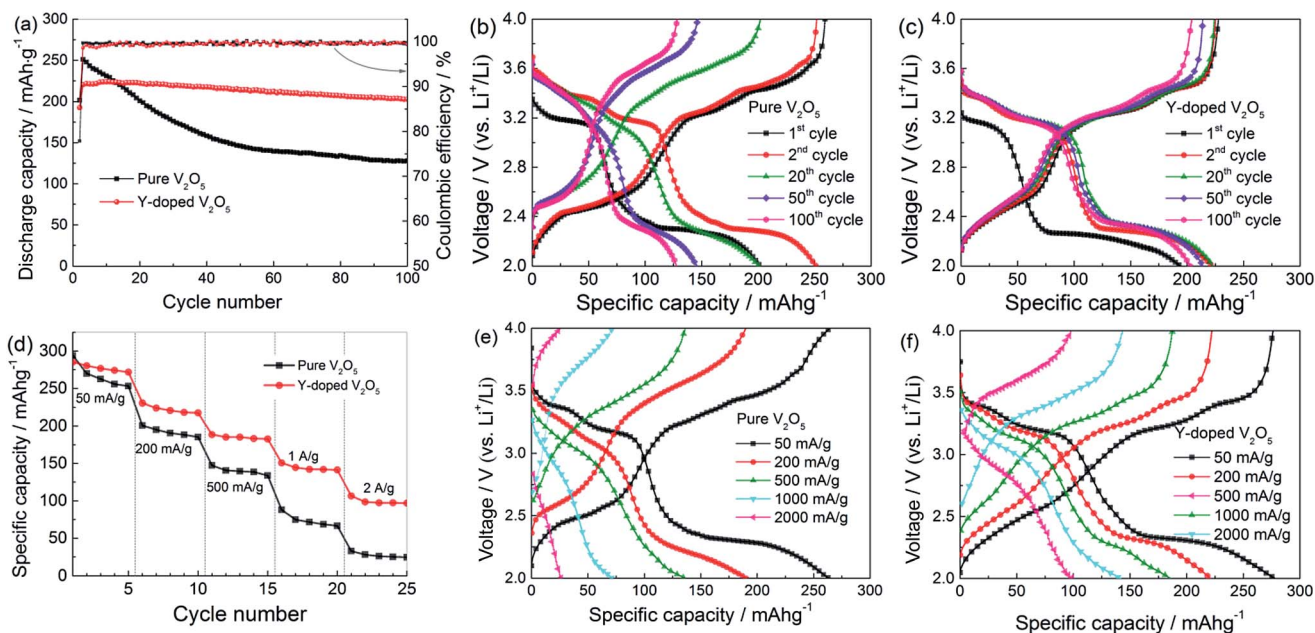
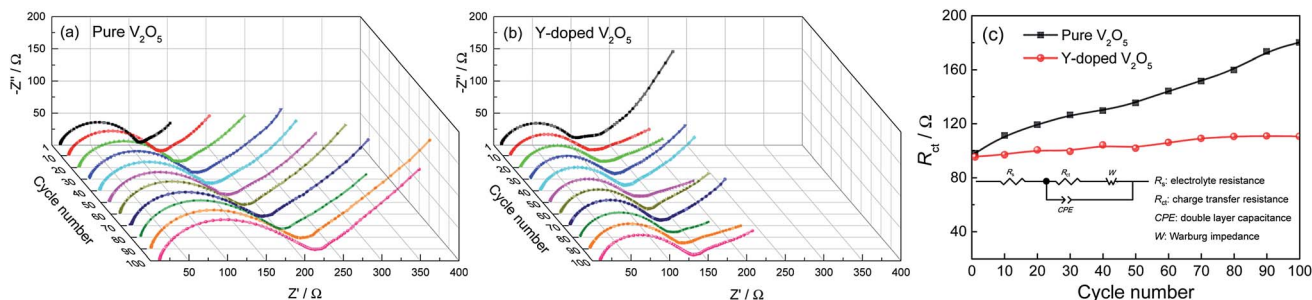


Fig. 7 (a) Cycling performance and (b, c) selected discharge/charge profiles at different cycles for the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes at a current density of  $200 mA g^{-1}$ . (d) Rate performance, and (e, f) the corresponding discharge/charge profiles at various current densities for the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes.



**Table 3** The summarization of electrochemical performance of the Y-doped  $V_2O_5$  in this work and other doped  $V_2O_5$  materials reported previously in the literatures

$V_2O_5$ materials	Voltage range/V	Current density/ $mA\ g^{-1}$	Maximum capacity/ $mA\ h\ g^{-1}$	Capacity retention/%	Ref.
Y-doped $V_2O_5$	2.0–4.0	200	224	91.6 (after 100 cycles)	This work
Cu-doped $V_2O_5$	2.0–4.0	58.8	242	69.0 (after 50 cycles)	31
Fe-doped $V_2O_5$	2.0–4.0	58.8	244	80.0 (after 48 cycles)	33
Cr-doped $V_2O_5$	2.0–4.0	150	196	86.7 (after 50 cycles)	34
		300	159	76.0 (after 50 cycles)	34
Al-doped $V_2O_5$	1.75–4.0	35	350	85.0 (after 20 cycles)	35
		350	208	70.0 (after 50 cycles)	35
Sn-doped $V_2O_5$	2.0–4.0	259	200	82.0 (after 50 cycles)	37



**Fig. 8** Nyquist plots of the (a) pure  $V_2O_5$  and (b) Y-doped  $V_2O_5$  electrodes after various discharge/charge cycles. (c) Variations of  $R_{ct}$  as a function of discharge/charge cycle number of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes at a current density of  $200\ mA\ g^{-1}$ . The electrical equivalent circuit is shown as an inset.

(decrease) of charge (discharge) voltage and the capacity gets reduced sharply. It is noticeable that the capacity loss with the plateau of about 3.2 V (corresponding to  $\epsilon/\delta$  transition) is much larger than those of others. Therefore, it can be inferred that the pure  $V_2O_5$  processes relatively poorer reversibility for Li intercalation with the voltage plateau of about 3.2 V ( $\epsilon/\delta$  transition), which is considered a main reason for the fast capacity fading. In contrast, for the Y-doped  $V_2O_5$  electrode, the discharge/charge voltage profile was well maintained since the second cycle, indicating an excellent capacity retention capability. Fig. 7d compares the rate performance of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes with discharge/charge rates from 50 to  $2000\ mA\ g^{-1}$ . As low rates, for example  $50\ mA\ g^{-1}$ , the pure  $V_2O_5$  displays a stable discharge capacity of  $256\ mA\ h\ g^{-1}$ , while the Y-doped  $V_2O_5$  electrode displays a stable discharge capacity of  $274\ mA\ h\ g^{-1}$ , indicating the specific capacity was improved by Y-doping. At higher rates, the superior capacity characteristics of the Y-doped  $V_2O_5$  electrode are even clearer. For example, at  $1000\ mA\ g^{-1}$ , the discharge capacity of the Y-doped  $V_2O_5$  electrode retains a capacity of  $142\ mA\ h\ g^{-1}$  in contrast to only  $68\ mA\ h\ g^{-1}$  for the pure  $V_2O_5$  electrode. Fig. 7e and f present the selected discharge/charge profiles of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes at various current densities. With the increase of current density, the discharge voltage decreases and the charge voltage increases due to the increasing polarization effect. For the Y-doped  $V_2O_5$  electrode, good reversible plateau regions can be observed at all the current densities. However, for the pure  $V_2O_5$  electrodes,

reversible plateau regions almost disappear when the current density is higher than  $500\ mA\ g^{-1}$ .

Fig. 8a and b give the Nyquist plots of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes after every ten discharge/charge cycles at the current density of  $200\ mA\ g^{-1}$ , respectively. The depressed semicircle observed at high frequency region is due to the charge transfer resistance ( $R_{ct}$ ); the inclined line at low frequency region relates to the Warburg impedance.<sup>59</sup> The  $R_{ct}$  values were determined by plot fitting with the equivalent circuit depicted in the inset in Fig. 8c. A constant phase element (CPE) is used in the equivalent circuit instead of a pure capacitance due to the inhomogeneous surface of the working electrode. Fig. 8c compares the evolutions of  $R_{ct}$  of the pure  $V_2O_5$  and Y-doped  $V_2O_5$  electrodes with cycling. Clearly, the  $R_{ct}$  of the pure  $V_2O_5$  electrode increases rapidly with cycling, while that of the Y-doped electrode increases very slowly. After one discharge/charge cycle, the  $R_{ct}$  values for the pure  $V_2O_5$  electrode ( $98.0\ \Omega$ ) is slightly higher than that ( $95.3$ ) for the Y-doped  $V_2O_5$  electrode. The  $R_{ct}$  value for the pure  $V_2O_5$  electrode enlarges drastically from  $98.0\ \Omega$  at the first cycle to  $180.1\ \Omega$  at the 100<sup>th</sup> cycle, whereas the  $R_{ct}$  value for Y-doped  $V_2O_5$  increase slowly from  $95.3\ \Omega$  at the first cycle to  $110.5\ \Omega$  at the 100<sup>th</sup> cycle, indicating that Y-doping has a positive effect on the depressing the charge transfer resistance during the process of discharge/charge cycles. The lower increase of impedance during cycling means smaller polarization and faster kinetics, which indicates good cycling stability and rate capability. These results are consistent with the superior electrochemical performance of Y-doped  $V_2O_5$ .



## 4. Conclusions

Y-doped  $V_2O_5$  was prepared by a facile sol-gel method combined with freeze drying technique followed with annealing in air. FE-SEM and XRD analysis revealed that this Y-doped  $V_2O_5$  has a sheet-like morphology and consists of small nanoparticles with the (110) preferred orientation. XPS tests demonstrated that Y doping induced more low valence state  $V^{4+}$  in  $V_2O_5$ . First-principles simulation indicated that Y dopant forms covalent bond with the adjacent O atoms within  $V_2O_5$  layers and decreases the strength of the neighbored V–O bonds. When used as cathode material for Li-ion batteries, the Y-doped  $V_2O_5$  exhibited much enhanced rate capability and cycling stability as compared to the pure  $V_2O_5$  counterpart. The superior lithium storage performance of the Y-doped  $V_2O_5$  could be ascribed to the following reasons: the nano-sized primary particles in Y-doped  $V_2O_5$  reduce the diffusion path of both  $Li^+$  and electrons, which benefits the improvement of rate capability; furthermore, the predominantly exposed (110) crystal planes of Y-doped  $V_2O_5$  provide channels for facile  $Li^+$  intercalation and deintercalation, which also contributes to the enhanced rate capability; the increased low valence state  $V^{4+}$  may improve the conductivity of Y-doped  $V_2O_5$  and decrease electrochemical reaction resistance; the chemical interaction between Y atom and the adjacent O atoms in the  $VO_5$  slabs could stabilize the layer structure of  $V_2O_5$  phase during electrochemical interaction of  $Li^+$ , allowing better structure stability during electrochemical cycling; the local structural defects caused by Y dopant may serve as possible nucleation centers for phase transformation during  $Li^+$  intercalation/deintercalation process and accordingly improve the kinetics of  $Li^+$  intercalation/deintercalation in Y-doped  $V_2O_5$  as well as its cycling performance.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 51664012, 51464009, and 51562006), Guangxi Natural Science Foundation of China (2015GXNSFGA139006), Postdoctoral Science Foundation of Central South University, and China Postdoctoral Science Foundation (2016M590754).

## Notes and references

- V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy Environ. Sci.*, 2011, **4**, 3243–3262.
- J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–367.
- Y. Tang, Y. Zhang, W. Li, B. Ma and X. Chen, *Chem. Soc. Rev.*, 2015, **44**, 5926–5940.
- N. Mahmood, T. Tang and Y. Hou, *Adv. Energy Mater.*, 2016, **6**, 1600374.
- P. Roy and S. K. Srivastava, *J. Mater. Chem. A*, 2015, **3**, 2454–2484.
- J. W. Fergus, *J. Power Sources*, 2010, **195**, 939–954.
- J. Xu, S. Dou, H. Liu and L. Dai, *Nano Energy*, 2013, **2**, 439–442.
- H. T. Tan, X. Rui, W. Sun, Q. Yan and T. M. Lim, *Nanoscale*, 2015, **7**, 14595–14607.
- D. McNulty, D. N. Buckley and C. O'Dwyer, *J. Power Sources*, 2014, **267**, 831–873.
- X. Huang, X. Rui, H. H. Hng and Q. Yan, *Part. Part. Syst. Charact.*, 2015, **32**, 276–294.
- Y. Wang and G. Cao, *Chem. Mater.*, 2006, **18**, 2787–2804.
- S. Tian, A. Xing, H. Tang, Z. Bao and G. Wu, *J. Mater. Chem. A*, 2014, **2**, 2896–2900.
- A. Q. Pan, J. G. Zhang, Z. M. Nie, G. Z. Cao, B. W. Arey, G. S. Li, S. Q. Liang and J. Liu, *J. Mater. Chem.*, 2010, **20**, 9193–9199.
- C. K. Chan, H. Peng, R. D. Twisten, K. Jarausch, X. F. Zhang and Y. Cui, *Nano Lett.*, 2007, **7**, 490–495.
- S.-L. Chou, J.-Z. Wang, J.-Z. Sun, D. Wexler, M. Forsyth, H.-K. Liu, D. R. MacFarlane and S.-X. Dou, *Chem. Mater.*, 2008, **20**, 7044–7051.
- D. Yu, C. Chen, S. Xie, Y. Liu, K. Park, X. Zhou, Q. Zhang, J. Li and G. Cao, *Energy Environ. Sci.*, 2011, **4**, 858–861.
- H.-g. Wang, D.-l. Ma, Y. Huang and X.-b. Zhang, *Chem. - Eur. J.*, 2012, **18**, 8987–8993.
- L. Mai, L. Xu, C. Han, X. Xu, Y. Luo, S. Zhao and Y. Zhao, *Nano Lett.*, 2010, **10**, 4750–4755.
- X. Rui, Z. Lu, H. Yu, D. Yang, H. H. Hng, T. M. Lim and Q. Yan, *Nanoscale*, 2013, **5**, 556–560.
- Z. l. Wang, D. Xu, L. m. Wang and X. b. Zhang, *ChemPlusChem*, 2012, **77**, 124–128.
- Y. Li, J. Yao, E. Uchaker, J. Yang, Y. Huang, M. Zhang and G. Cao, *Adv. Energy Mater.*, 2013, **3**, 1171–1175.
- D.-J. Yan, X.-D. Zhu, K.-X. Wang, X.-T. Gao, Y.-J. Feng, K.-N. Sun and Y.-T. Liu, *J. Mater. Chem. A*, 2016, **4**, 4900–4907.
- J. Liu, Y. Zhou, J. Wang, Y. Pan and D. Xue, *Chem. Commun.*, 2011, **47**, 10380–10382.
- J. Wang, H. Tang, L. Zhang, H. Ren, R. Yu, Q. Jin, J. Qi, D. Mao, M. Yang, Y. Wang, P. Liu, Y. Zhang, Y. Wen, L. Gu, G. Ma, Z. Su, Z. Tang, H. Zhao and D. Wang, *Nat. Energy*, 2016, **1**, 16050.
- E. Uchaker, N. Zhou, Y. Li and G. Cao, *J. Phys. Chem. C*, 2013, **117**, 1621–1626.
- G. Li, Y. Qiu, Y. Hou, H. Li, L. Zhou, H. Deng and Y. Zhang, *J. Mater. Chem. A*, 2015, **3**, 1103–1109.
- S. Zhou, X. Yang, Y. Lin, J. Xie and D. Wang, *ACS Nano*, 2012, **6**, 919–924.
- H. B. Wu, J. S. Chen, H. H. Hng and X. Wen Lou, *Nanoscale*, 2012, **4**, 2526–2542.
- Q. Zhang, E. Uchaker, S. L. Candelaria and G. Cao, *Chem. Soc. Rev.*, 2013, **42**, 3127–3171.
- M. Wagemaker and F. M. Mulder, *Acc. Chem. Res.*, 2013, **46**, 1206–1215.
- H. Yu, X. Rui, H. Tan, J. Chen, X. Huang, C. Xu, W. Liu, Y. Denis, H. H. Hng and H. E. Hoster, *Nanoscale*, 2013, **5**, 4937–4943.
- D. Yu, S. Zhang, D. Liu, X. Zhou, S. Xie, Q. Zhang, Y. Liu and G. Cao, *J. Mater. Chem.*, 2010, **20**, 10841–10846.
- S.-R. Li, S.-Y. Ge, Y. Qiao, Y.-M. Chen, X.-Y. Feng, J.-F. Zhu and C.-H. Chen, *Electrochim. Acta*, 2012, **64**, 81–86.



- 34 S. Zhan, C. Wang, K. Nikolowski, H. Ehrenberg, G. Chen and Y. Wei, *Solid State Ionics*, 2009, **180**, 1198–1203.
- 35 Y. L. Cheah, V. Aravindan and S. Madhavi, *Electrochim. Acta*, 2012, **4**, 3270–3277.
- 36 Y. Li, J. Yao, E. Uchaker, M. Zhang, J. Tian, X. Liu and G. Cao, *J. Phys. Chem. C*, 2013, **117**, 23507–23514.
- 37 Z. Li, C. Zhang, C. Liu, H. Fu, X. Nan, K. Wang, X. Li, W. Ma, X. Lu and G. Cao, *Electrochim. Acta*, 2016, **222**, 1831–1838.
- 38 C. M. Carbonaro, D. Chiriu and P. C. Ricci, *Phys. Status Solidi C*, 2016, **13**, 1017–1022.
- 39 N. Zhao, Y. Li, X. Zhi, L. Wang, X. Zhao, Y. Wang and G. Liang, *J. Rare Earths*, 2016, **34**, 174–180.
- 40 L. Wang, C. Jiao, G. Liang, N. Zhao, Y. Wang and L. Li, *J. Rare Earths*, 2014, **32**, 895–899.
- 41 Z. Lan, J. Li, B. Wei, R. Zhu and J. Guo, *J. Rare Earths*, 2016, **34**, 401–406.
- 42 C. J. Fontenot, J. W. Wiench, M. Pruski and G. L. Schrader, *J. Phys. Chem. B*, 2000, **104**, 11622–11631.
- 43 M. D. Segall, J. D. L. Philip, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717.
- 44 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 45 K. Laasonen, R. Car, C. Lee and D. Vanderbilt, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1991, **43**, 6796–6799.
- 46 M. Giorgetti, M. Berrettoni and W. H. Smyrl, *Chem. Mater.*, 2007, **19**, 5991–6000.
- 47 J. H. Zheng, J. L. Song, Q. Jiang and J. S. Lian, *Appl. Surf. Sci.*, 2012, **258**, 6735–6738.
- 48 D. Liu, Y. Liu, A. Pan, K. P. Nagle, G. T. Seidler, Y.-H. Jeong and G. Cao, *J. Phys. Chem. C*, 2011, **115**, 4959–4965.
- 49 R. Enjalbert and J. Galy, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1986, **42**, 1467–1469.
- 50 M. D. Segall, R. Shah, C. J. Pickard and M. C. Payne, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 16317–16320.
- 51 C. Delmas, H. Cognac-Auradou, J. M. Cocciantelli, M. Ménétrier and J. P. Doumerc, *Solid State Ionics*, 1994, **69**, 257–264.
- 52 X. Li, C. Liu, C. Zhang, H. Fu, X. Nan, W. Ma, Z. Li, K. Wang, H. Wu and G. Cao, *ACS Appl. Mater. Interfaces*, 2016, **8**, 24629–24637.
- 53 R. Baddour-Hadjean, A. Marzouk and J. P. Pereira-Ramos, *J. Raman Spectrosc.*, 2012, **43**, 153–160.
- 54 H. Zhao, L. Pan, S. Xing, J. Luo and J. Xu, *J. Power Sources*, 2013, **222**, 21–31.
- 55 J. P. Pereira-Ramos, P. Soudan, R. Baddour-Hadjean and S. Bach, *J. Power Sources*, 2011, **196**, 1392–1398.
- 56 W. Ma, C. Zhang, C. Liu, X. Nan, H. Fu and G. Cao, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19542–19549.
- 57 S. Zhan, C. Wang, G. Chen, F. Du and Y. Wei, *Ionics*, 2010, **16**, 209–213.
- 58 S. Zhan, G. Chen, D. Liu, A. Li, C. Wang and Y. Wei, *J. Alloys Compd.*, 2009, **479**, 652–656.
- 59 Y. W. Li, J. H. Yao, C. J. Liu, W. M. Zhao, W. X. Deng and S. K. Zhong, *Int. J. Hydrogen Energy*, 2010, **35**, 2539–2545.

