Li_{2.97}Mg_{0.03}VO₄: High Rate Capability and Cyclability Performances

Anode Material For Rechargeable Li-ion batteries

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Abstract

Mg-doped composite, Li_{2.97}Mg_{0.03}VO₄, with an orthorhombic structure was prepared by a sol-gel method. The effects of the Mg doping on the structure and electrochemical performance of Li₃VO₄ were investigated. The X-ray diffraction pattern shows that the Mg doping does not change the crystal structure of Li₃VO₄. The EDS mappings indicated the fairly uniform distribution of Mg throughout the grains of Li_{2.97}Mg_{0.03}VO₄. Electronic conductivity of Mg-doped Li₃VO₄ increased by two orders of magnitude compared to that of pure Li₃VO₄. CV and EIS measurement confirms that the Li_{2.97}Mg_{0.03}VO₄ sample exhibits a smaller polarization and transfer

resistance and a higher lithium diffusion coefficient compared with the pure Li_3VO_4 . Due to the better electrochemical kinetics properties, Mg-doped Li_3VO_4 showed a significant improved performance compared to the pure Li_3VO_4 , especially for the high rate capability. At the higher discharge/charge rate (2C), the discharge and charge capacities of 415.5 and 406.1 mAh/g have been obtained for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ which is more than three times higher the discharge/charge capacities of Li_3VO_4 . The discharge and charge capacities of pure Li_3VO_4 are only 126.4 and 125.8 mAh/g respectively. The excellent electrochemical performance of $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ enables it as a promising anode material for rechargeable lithium-ion batteries.

Keywords: anode materials; Mg-doping; rate capability.

1. Introduction

Graphite/Carbon-based materials widely used as anode materials in lithium-ion batteries. Graphite with a theoretical specific capacity of 372 mAh g^{-1} is a typical representative anode for lithium-ion batteries. However, due to its low operating potential ($\sim 0.2 \text{ V}$ vs. Li^+/Li), graphite suffers severe safety issue such as dendritic lithium growth. Especially at high rates, polarization further lowers its operating voltage, causing the birth of new lithium dendrites and the consequent safety issues [1, 2]. In an attempt to develop new alternatives anode materials for lithium-ion batteries, oxide-based materials have recently received a lot of attention [3]. Representative oxide anode for lithium-ion batteries is spinel structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can intercalate three lithium ions per formula and the reversible charge/discharge

capacities close to the theoretical value (175 mAh/g). The excellent cyclic stability along with nearly no volume change during the intercalation/de-intercalation process was reported for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [4-6]. However, due to the relatively high lithium insertion potential (~1.5 V) in comparison with that of ~0.2 V for graphite, it significantly reduces the overall operating cell voltage and that is why the advantage of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ itself cancels the benefits of high voltage oxide cathode materials.

Recently, it has been reported that Li_3VO_4 can be used as a potential anode for Li-ion batteries. As an intercalation electrode, it is successful because of the small structural and volume changes and the fast movement of Li ions across the lattice. Compared with other intercalation electrodes, it intercalates Li ions at a voltage mainly between 0.5–1.0 V versus Li^+/Li , lower than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and higher than the dendrite formation voltages. This makes Li_3VO_4 much safer anode than graphite [7-9]. Due to its safe operating voltage and large specific capacity, Li_3VO_4 might play a promising role as a new intercalation anode for Li-ion batteries. In spite of these advantages, Li_3VO_4 as an anode material still meets some drawbacks when it comes to practical implementation. Li_3VO_4 is an excellent ionic conductor, but the band gap of 3.9 eV gives an insulating character to this material [10]. The rather low electronic conductivity compared to its ionic conductivity causes the large resistance polarization and poor rate capability for Li_3VO_4 as an anode material for lithium-ion batteries. Considerable efforts were made to overcome the drawback and improve the electrochemical performance of Li_3VO_4 . W. T. Kim prepared the single phase Li_3VO_4 powder by solution-based method. Compared with traditional solid-state method, the

significant reduction of the particle size of the Li_3VO_4 lead to an excellent cyclability [11]. Z. Liang synthesized the carbon-coated Li_3VO_4 by sol-gel method. The carbon-coated Li_3VO_4 exhibited a very high reversible capacity and good rate capability [12]. Y. Shi et. al synthesized the hollow structured Li_3VO_4 and used graphemeas 3D electric network coating with hollow structure to improve the conductivity. This also significantly improved the electrochemical performance of the Li_3VO_4 [13]. In addition, combining carbon coating and nanotechnology are also used to synthesize the high-performance Li_3VO_4 anode materials. T. Zhai prepared the carbon-coated nano Li_3VO_4 particles [14]. J. Liu synthesized the ultrathin Li_3VO_4 nanoribbon/graphene sandwich-like nanostructures [15]. Although, above mentioned methods improved the electrochemical performance by reduce the particle size and/or coating of the conducting carbonon the surface, the intrinsic electronic conductivity of the Li_3VO_4 have not been improved and a big fat polarization still exist.

The doping methods have been proved to be a direct and efficient way to alter the intrinsic electronic proerty of battery materials. Chung et al. found that by doping aliovalent metal ion to Li site, the electronic conductivity of the LiFePO_4 can be increased by a factor of $\sim 10^8$. The resulting materials show near-theoretical energy density at low charge/discharge rates and can retain significantly high capacity with little polarization at higher rates [16]. Qiu et al. reported that doping Mg in tetrahedral 8a Li^+ site and Zr in octahedral 16d Ti^{4+} site in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ breaks the charge balance due to unequal valances compared with corresponding substituted elements. As a result, some electrons will be generated to compensate the unbalanced charge, and the

intrinsic electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is significantly improved, leading to enhanced rate capability [17]. It is reasonable to believe that doping of aliovalent metal ion in Li site should be an efficient way to improve the electrochemical performance of the Li_3VO_4 . Considering the similar ion radius with Li-ion, here we used the divalent magnesium as the doping elements and the single phase $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ compound was successfully synthesized by a sol-gel method for the first time. In this paper, we present the structural properties, morphology, electronic conductivity characterizations and electrochemical performance of pure and Mg-doped Li_3VO_4 by means of X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) images, Cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS).

2. Experimental

Mg-doped Li_3VO_4 , $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$, was prepared by a sol-gel method using citric acid and the required amounts of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, V_2O_5 , $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as starting materials. Citric acid was employed as both a chelating reagent and a carbon source coated on the samples in this sol-gel process and it was added in a molar ratio of 1:1 (citric acid: V). First, $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ was dissolved in deionized water to form a colorless transparent solution, then V_2O_5 , $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, citric acid were added into the solution in turns with continuous stirring at 50 °C for 0.5 h to form an orange solution. The solution was heated gently with continuous stirring to remove the excess water at 80°C in a thermostatic water bath. After drying at 80°C in an air oven, the gel was transferred into an alumina boat and then heated at 350°C for

5h under a stream of reducing atmosphere (95%Ar + 5%H₂). The resulting powder was grounded and pressed into pellets, and then was heated again at a rate of 2°C/min to 650°C and held for 5 h under the same reducing atmosphere. Before removing from the furnace, the samples were slowly cooled down to room temperature. An un-doped sample of Li₃VO₄ was also prepared by the same route.

Powder X-ray diffraction (XRD) patterns of the products were recorded at room temperature with a Philips X-ray diffractometer equipped with Cu K_α radiation in a continuous-scanning mode. For XRD refinement, data was collected by a step-scanning mode over the range 10-90° with a step size of 0.02° and a dwell time of 2 s. Rietveld refinement was performed using the FullProf program to obtain the crystal structure parameters. The morphologies of the samples were examined by a JEOLJSM-5610 and FEI Strata TMDB235 SEM/FIB microscope.

For electrochemical measurements, the anode was prepared by mixing the as-prepared samples with acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 85:10:5 in N-methyl-2-pyrrolidone (NMP). The obtained slurry was coated onto copper foil current collector, dried at 50 °C for 24h and pressed (5 MPa) respectively. Then, the electrodes fabricated were dried again at 90 °C for 12h in a vacuum and cut into disc with a diameter of 14 mm using a punch where about 5 mg of active materials was hold on it. Coin cells were assembled in a Mikrouna glove box filled with high-purity argon, where the lithium metal foil were used as the counter electrode, Celgard® 2320 as a separator, and 1M LiPF₆ in EC:DMC (1:1 vol.%) were used as an electrolyte. The electrochemical performance of the prepared

samples was evaluated with the coin cell by an automatic battery tester system (Land®, China) at room temperature and the electrochemical capacity of samples was evaluated based only on the active material weight.

Cyclic voltammetric (CV) tests, Electrochemical impedance spectroscopy (EIS) and Electronic conductivity were performed on an Autolab PGSTAT100 type electrochemical workstation (Metrohm AG company) respectively. CV tests were carried out at a scan rate of 0.05 mVs^{-1} on the potential interval 0.1-3.0 V (vs. Li^+/Li). All tests were performed at room temperature. The impedance spectra were recorded by applying an ac voltage of 5 mV in the frequency range from 1 MHz to 0.01 HZ. Pellets used for the electronic conductivity measurement were prepared by die-pressing the powder samples and firing at 600°C for 5h under a stream of reducing atmosphere (95%Ar + 5%H₂). The size of the pellets was around 0.8 cm in diameter and 0.06 cm in thickness. Then a silver conductor paste was coated on both sides of the pellets to form the blocking electrodes. The electronic conductivity measurement was measured by linear voltage scanning method at a scanning rate of 1 mV/s from 0 to 0.2 V.

3. Results and discussion

XRD patterns of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples are shown in Fig. 1. For comparison, the data of the position and the relative intensity of the peaks of crystalline Li_3VO_4 sample (JCPDF No. 38-1247) are also shown in the bottom of the figure. From Fig. 1, we can see that the Mg-doped sample gave a very similar diffraction profile to that of Li_3VO_4 . All diffraction peaks of the two patterns could be

fully indexed into an orthorhombic structure, space group $Pmn21$, with the program Dicvol, and no impurities were detected in the pattern.

Fig. 1 XRD patterns of Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples.

In order to further explore the structural change affected by the Mg doping, a Rietveld refinement was conducted for two samples. The refinement results shown in Fig. 2 led to a good agreement between the experimental and the calculated XRD pattern. The reasonably small R_{wp} factor (10.4% for Li_3VO_4 and 11.1% for $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$) suggests that single phase compounds were obtained and no impurity phases were detected under the resolution of our X-ray diffractometer. The structural parameters of $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ obtained from the refinement are listed in Table 1. We can see that the Mg mainly occupy Li site in the Mg-doped sample. The occupancy of Mg are 0.0181 and 0.0094 for Li1 site and Li2 site, respectively. The lattice parameters calculated by refining the XRD patterns are shown in Table 2.

Fig. 2 The refinement results of the Li_3VO_4 sample

(a) and the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample (b).

Table 1 Structure parameters of $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ determined from X-ray diffraction

Atoms	Site	x	y	z	Occupancy
Li1	4b	0.2426(2)	0.1701(1)	0.4534(5)	0.9819(7)
Mg1	4b	0.2426(2)	0.1701(1)	0.4534(5)	0.0181(7)
Li2	2a	0.0000	0.6608(4)	0.5281(2)	0.4906(4)
Mg2	2a	0.0000	0.6608(4)	0.5281(2)	0.0094(4)
V	2a	0.0000	0.3293(3)	0.0047(7)	0.50
O1	4b	0.2323(7)	0.1814(8)	0.0679(2)	1.00
O2	2a	0.0000	0.6325(4)	0.0702(7)	0.50
O3	2a	0.0000	0.3312(9)	0.6224(6)	0.50

Table 2 The lattice parameters for Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	V (Å ³)
Li_3VO_4	6.323(2)	5.444(3)	4.947(1)	170.32
$\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$	6.324(4)	5.445(2)	4.949(3)	170.41

Because of the similar ionic radius of Mg^{2+} (0.57 Å) and Li^+ (0.59 Å) in tetrahedral coordination, the lattice parameters for Mg-doped sample remained unchanged to that of Li_3VO_4 sample. These observations indicate that the Mg^{2+} ions have been successfully introduced into the lattice Li sites of Li_3VO_4 and do not change its structural characteristics.

Fig 3(a) and (b) present the SEM images of Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples. For pure Li_3VO_4 , the sample present a bigger particle size and a aggregated structure, while for the Mg-doped sample, slightly smaller particles size and a reduced

agglomeration can be observed.

Fig. 3 The SEM images of (a) Li_3VO_4 sample; (b) $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples and The EDS mappings of (c) V; (d) O; (e) Mg and (f) C for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample

In order to see if the doped Mg element is uniformly dispersed in the Li_3VO_4 bulk,

we analyzed the elemental mapping of the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples by the EDS measurement. The EDS mappings indicate that like the elements V, O and C, the substituted Mg have a fairly uniform distribution in $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ (Fig. 3).

Fig. 4 The typical charge/discharge voltage profile of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples for the initial three cycles.

Fig. 4 shows the typical charge/discharge voltage profiles of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples for the initial four cycles in the potential range of 0.1 to 3 V at 0.1C rate. From this figure, we can see that the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample gave a similar charge/discharge voltage profiles to that of Li_3VO_4 . For both Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples, from first to second charge/discharge cycles, a big capacity lost can be observed. The irreversible capacity lost can be attributed to the side

Fig. 5 The CV profile of the Li_3VO_4 (a) and the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ (b) samples.

reactions such as formation of solid electrolyte interface (SEI) film and

decomposition of electrolyte [18, 19]. In addition, after the first cycle, both of the two samples showed a stable and good cycling performance. However, for the Mg-doped sample and the pure Li_3VO_4 samples, the obviously difference in the charge/discharge voltage profile can also be observed. Firstly, for Mg-doped sample, the initial discharge voltage profile presents more voltage plateau which can be seen more clearly from CV profiles (See Fig. 5). Secondly, the charge/discharge capacity of the Mg-doped sample is obviously higher than that of the Li_3VO_4 sample for the corresponding cycles. The initial discharge and charge capacities are 655 and 499 mAh/g for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$. However for the pure Li_3VO_4 , the values are only 575 and 451 mAh/g respectively. Finally, compared with the pure Li_3VO_4 , the Mg-doped sample showed a smaller resistance polarization as observed by the voltage gap between charge and discharge. The reduced polarization can also be confirmed by the CV measurements.

Fig. 5 shows the first four CV cycles of the Li_3VO_4 (a) and the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ (b) samples at a scan rate of 0.05 mV s^{-1} on the potential range of 0.1~3V. From this figure, several obvious differences can be observed for the two samples. Firstly, the number of the reduction peaks are different in the 1st cathodic scan curves. For the Li_3VO_4 , the CV curves show two reduction peaks at 0.418 and 0.472 V. However, the three obviously reduction peaks at 0.391, 0.546 and 0.663 V are observed for $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample. Those reduction peaks appeared in the 1st cathodic scan are usually attributed to the lithiation process owing to the reduction of Li_3VO_4 and the occurrence of the side reactions on the electrode surfaces and interfaces due to the

formation of the SEI. Therefore, for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample, due to the influence of doped Mg, there may be exist a different SEI formation mechanism. Secondly, for the two samples, after first cycle, although the CV curves show the similar profile which represent two reduction peaks and an oxidation peak, the change in the potential difference between these two peaks can be observed. Table 3 listed the differences between the reduction peaks and an oxidation peaks of the Li_3VO_4 electrode and the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrode after first cycle. From this table, we can see that the potential difference of the Mg-doped Li_3VO_4 electrode is lower than that of the pure Li_3VO_4 electrode for the corresponding cycles. At the second cycle, the potential differences between the oxidation and reduction peaks are 0.793 V and 0.437 V for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$. However for the pure Li_3VO_4 , the values are only 0.875 V and 0.463 V respectively. After 4 cycles, the values are 0.715 V and 0.289 V for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ which is still lower than of the pure Li_3VO_4 , where the values for Li_3VO_4 are 0.753 V and 0.439 V respectively. The potential difference between the reduction peaks and an oxidation peaks can reflect the degree of the polarization of the electrode [20]. For the Mg doped Li_3VO_4 sample, the cause of the reduced polarization should be attributed to the improvement of the electronic conductivity (see Fig. 7). The significant reduced polarization suggested that Mg doping also enhanced the reversibility of the Li_3VO_4 .

Table 3 The potential differences between the oxidation and reduction peaks of the Li_3VO_4 electrode and the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrode after first cycle.

Sample	cycle	φ_o (V)	φ_{r1} (V)	φ_{r2} (V)	ΔE_1 (V)	ΔE_2 (V)
Li_3VO_4	2 nd cycle	1.335	0.457	0.872	0.878	0.463
	3 rd cycle	1.319	0.544	0.923	0.775	0.396
	4 th cycle	1.301	0.548	0.952	0.753	0.349
$\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$	2 nd cycle	1.324	0.531	0.887	0.793	0.437
	3 rd cycle	1.286	0.567	0.987	0.719	0.299
	4 th cycle	1.284	0.569	0.995	0.715	0.289

φ_o — the oxidation peak; φ_{r1} — the first reaction peak; φ_{r2} — the second reaction peak;

$\Delta E_1 = \varphi_o - \varphi_{r1}$; $\Delta E_2 = \varphi_o - \varphi_{r2}$

Fig. 6 The cycle performance of the Li_3VO_4 and the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples at different discharge rates (0.1C, 0.2C, 0.5C, 1C and 2C) at room temperature

The cycle performance of the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample is given in Fig. 6. In order to investigate the rate capability during cycling, various current rates of 0.1C, 0.2C, 0.5C, 1C and 2C were applied to the working electrode. Obviously, after first cycle, the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample has a much higher reversible capacity than Li_3VO_4 at

different discharge rates. The discharge and charge capacities at 0.1C are 497.9 and 493 mAh/g for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ for the second cycle. However for the pure Li_3VO_4 , the values are only 476.6 and 447.3 mAh/g respectively. Especially at the higher discharge rate 2C, the discharge and charge capacities of 415.5 and 406.1 mAh/g have been obtained for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ which is more than three times higher the discharge/charge capacities of Li_3VO_4 . Where for the pure Li_3VO_4 , the discharge and charge capacities are only 126.4 and 125.8 mAh/g respectively. It should be emphasized that the discharge and charge specific capacities of the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrode can be completely recovered when 0.1C current rate was applied again. In addition, compared with the pure Li_3VO_4 , the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrode show an inspiring rate cycle stability. Except for the first cycle, the discharge and charge capacities remain almost unchanged at the same current rate. At 0.1C rate, the discharge and charge capacities for the 2nd and 10th cycles of the pure Li_3VO_4 are 476.6, 447.3 and 373.3, 375.1 mAh/g, respectively, and the mean fade of the capacities are 2.4% and 1.8% per cycle; the mean fade of the capacities of the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ are only 0.16% and 0.14% per cycle. Even at a higher rate, the cycle performance shows good improvement for the Mg-doped sample. The obviously improvement of the electrochemical performance indicates substantially enhanced electronic conductivity and electrochemical kinetics of lithium-ion extraction/insertion from/into $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$, which was confirmed by the V/I curves and the electrochemical impedance measurement as shown in Fig. 7 and Fig. 8.

Fig. 7 The V/I curves of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ pellets

Table 4 The calculated electronic conductivities of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples by V/I curves

Sample	Li_3VO_4	$\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$
Pellet thickness /cm	0.058	0.058
Diameter /cm	0.8	0.8
σ_e from linear voltage scan / S cm^{-1}	1.66×10^{-10}	4.37×10^{-8}

Table 5 Impedance parameters of Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrodes

Sample	$R_s (\Omega)$	$R_{ct} (\Omega)$	$W (\Omega)$	$\sigma (\Omega \text{ s}^{-0.5})$	$D (\text{cm}^2 \text{ s}^{-1})$
Li_3VO_4	1.5	2014.1	1016.3	355.9	1.24×10^{-8}
$\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$	1.9	832.1	461.4	237.0	4.03×10^{-8}

The electronic conductivities of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples were measured by the linear voltage scanning method. From Fig. 7 we can see that the V/I curves represent a significant linear relationship for both samples. However, an obviously small slop of the V/I curve for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample shows that Mg

doping in lithium site improved the electronic conductivity of the Li_3VO_4 material.

Fig. 8 (a) the EIS plots of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrodes and

(b) the linear fitting of the Z_{re} Vs. $\omega^{-1/2}$ relationship.

The calculated electronic conductivities of the Li_3VO_4 and $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ samples by V/I curves are listed in [table 4](#). The electronic conductivity is $1.66 \times 10^{-10} \text{ S cm}^{-1}$ for the pure Li_3VO_4 . However, for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample, the value is $4.37 \times 10^{-8} \text{ S cm}^{-1}$. The electronic conductivity of the Li_3VO_4 was increased by two orders of magnitude after Mg doping. Li_3VO_4 is an excellent ionic conductor, however, the band gap energy of 3.9 eV gives an insulating character to this material. Mg-doped Li_3VO_4 leads to significantly improved electrical conductivity and therefore greatly enhanced the electrochemical performance compared to the pure Li_3VO_4 .

EIS plots of the pure Li_3VO_4 and Mg-doped Li_3VO_4 electrodes were recorded at room temperature (Fig. 8 (a)). The shapes of the EIS plots for the two samples are similar composed of one semicircle in the high frequency region and a sloping line in the low frequency region. An equivalent circuit model, as shown in the inset figure, can be employed to fit the EIS patterns and the fitted impedance parameters are listed in [Table 5](#). The fitting data are in good agreement with experimental data as shown in Fig. 8 (b). In the equivalent model, the R_s is the total resistance of the battery including the ionic resistance of the electrolyte, the intrinsic resistance of the active material, and the contact resistance at the interface active material/current collector. A constant phase element (CPE) associated with the interfacial resistance. R_{ct} , the semi-circle, is correlated with the charge transfer resistance and W , the linear portion, represents the Warburg diffusion impedance. [Table 5](#) shows that the charge transfer resistance of the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrode is much lower than that of the Li_3VO_4 , indicating that the Mg-doping reduces the resistance, enhances the charge transfer

across the electrode-electrolyte interface. It can be believed that the low R_{ct} value corresponds to the material's small electrochemical polarization. So Mg doping reduced the electrochemical polarization of Li_3VO_4 and lead to a better cyclic rate performance which can be reflected from CV curves (Fig. 5) and the electrochemical performance (Fig. 6).

The lithium diffusion coefficient (D_{Li}) can be calculated from the Warburg region using the following equation [21]:

$$D_{\text{Li}} = \frac{1}{2} \left[\left(\frac{V_m}{FS\sigma} \right) \left(-\frac{dE}{dx} \right) \right]^2 \quad [1]$$

where V_m is the molar volume of Li_3VO_4 , F is the Faraday constant, S is the surface area of the electrode, the value of dE/dx is the slop of the open-circuit potential vs. Li ion concentration x and σ is the Warburg factor which is related to Z_{re} obeying the following relationship:

$$Z_{\text{re}} = R_{ct} + R_s + \sigma \omega^{-\frac{1}{2}} \quad [2]$$

the slope σ can be obtained based on the linear fitting of Z_{re} Vs. $\omega^{-1/2}$ as shown in the Fig. 8 (b). Using the equation [1] and [2], the lithium diffusion coefficient value of the Li_3VO_4 is calculated to be 1.24×10^{-8} , while for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$, the value is $4.03 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ which is obvious higher than that of the Li_3VO_4 .

The EIS measurement results also indicated that the Mg-doped Li_3VO_4 sample has smaller charge transfer resistance and higher lithium diffusion coefficient, which are favorable for improving the electrochemical kinetics. These results are in accordance with the electrochemical measurement results (Fig. 6).

4. Conclusions

$\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample was successfully synthesized for the first time by a sol-gel method. The X-ray diffraction pattern and Rietveld refinement result showed that the Mg doping in Li_3VO_4 did not change the crystal structure of the Li_3VO_4 . The V/I curve show that, by Mg doping on Li site, the electronic conductivity of the Li_3VO_4 can be increased by two orders of magnitude from $1.66 \times 10^{-10} \text{ S cm}^{-1}$ for the pure Li_3VO_4 to $4.37 \times 10^{-8} \text{ S cm}^{-1}$ for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$. As a result, the electrochemical kinetics of the electrode in term of polarization and charge transfer, as well as lithium ion diffusion and even rate capability and capacity retention are significantly improved. CV tests show that compared with the pure Li_3VO_4 , the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample exhibit a smaller polarization. The EIS measurement results indicated that for $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ sample, a smaller transferresistance and higher lithium diffusion coefficient was obtained. At the higher discharge/charge rate 2C, the discharge and charge capacities of 415.5 and 406.1 mAh/g have been obtained for the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ which is more than three times higher the discharge/charge capacities of Li_3VO_4 . In addition, compared with the pure Li_3VO_4 , the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ electrode show an inspiring rate cyclic stability. Except for the first cycle, the discharge and charge capacities remain almost unchanged at the same current rate. At 0.1C rate, the discharge and charge capacities for the 2nd and 10th cycles of the pure Li_3VO_4 are 476.6, 447.3 and 373.3, 375.1 mAh/g, respectively, and the mean fade of the capacities are 2.4% and 1.8% per cycle; However, the mean fade of the capacities of the $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ are only 0.16% and 0.14% per cycle. The excellent electrochemical performances of $\text{Li}_{2.97}\text{Mg}_{0.03}\text{VO}_4$ enables it as a promising anode

material for rechargeable Lithium-ion batteries.

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