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Insights into the Mg storage property and mechanism based on the honeycomb-like structured $Na_3V_2(PO_4)_3/C/G$ in anhydrous electrolyte



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- A honeycomb-like structured NVP/C/ G is constructed by a convenient and universal spray-drying method.
- The ED-NVP/C shows faster diffusion kinetics during demagnesiation process.
- The R_{ct} shows a positive relationship to the formation of NaV₂(PO₄)₃ phase.
- A Mg full cell prototype based on the ED-NVP/C/G cathode and Mg metal anode is proposed.

ARTICLEINFO

Keywords: Honeycomb-like structure Na₃V₂(PO₄)₃ Mg storage Mechanism Mg full cell



ABSTRACT

The high-voltage cathode material based on the sodium super ionic conductor (NASICON) structured Na₃V₂(PO₄)₃ (NVP) has been found to be a potential candidate for Mg storage. In this work, to improve its electrochemical performance, we construct honeycomb-like structured NVP/C/G with faster electronic and ionic transport by a convenient and universal spray-drying method for the first time. After electrochemically desodiating two Na from the NVP/C/G (ED-NVP/C/G), the ED-NVP/C/G is tested in highly anhydrous Mg electrolyte, and the insights into its Mg storage property and mechanism are carefully studied. An initial capacity of 87 mAh g⁻¹ with a relatively high average discharge voltage of 2.47 V vs. Mg²⁺/Mg is obtained at 0.1 C. The Xray diffraction (XRD) results show that the inserted Mg²⁺ ions tend to occupy the Na2 (at 18e sites) vacant sites. The investigation of kinetic process by galvanostatic intermittent titration technique (GITT) reveals that the Mg diffusion kinetics is faster during the demagnesiation process. The electrochemical reaction of NaV₂(PO₄)₃ phase. Finally, a Mg full cell prototype based on the ED-NVP/C/G cathode with Mg metal anode is built. The rational structure design of NVP/C/G improves the electrochemical performance for Mg storage, and our work also gives new understanding into the Mg storage mechanism in the ED-NVP/C/G structure.

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1. Introduction

The applications of lithium ion batteries (LIBs) in large scale energy storages are hindered by the high cost and safety problems. Although post-LIBs such Li-S batteries are developed, they are still Li-based electrochemical systems [1,2]. Due to the scarcity and uneven distribution of Li resources, the post-LIBs based on non-Li systems, such as Na/Mg/Al/Ca-based batteries, are attracted increasingly attention as alternatives for LIBs. For example, sodium ion batteries (SIBs) become a shining star benefiting from its low cost. However, unlike multivalent metal. Na metal is not suitable to be used as an anode due to the safety problems. Although researches focus on anode materials such as TiO₂, allovs and carbon materials, and polymer electrolyte with better safety properties have been done, the electrochemical performance of the full cell still needs further improvement for commercialization [3-8]. On the other hand, to improve the energy density, using metals as the anode is an effective strategy since they usually possess low reduction potential and high energy density (Fig. S1). For instance, Ca^{2+}/Ca exhibits a relatively low potential of -2.86 V vs. S.H.E., and the moderate charge density of Ca²⁺ may allow faster diffusion than other multivalent ions, making it a promising post-LIBs. However, the electrolyte that allow reversible Ca stripping/deposition is very rare at room temperature (RT), resulting in the difficulty to build a full cell [9,10]. Among the multivalent ion batteries, rechargeable Mg batteries (RMBs) possesses prominent overall advantages: (i) The deposition of Mg tends to be dendrite-free due to its low diffusion barrier, making it a safe anode [11]; (ii) The low reduction potential of Mg (-2.37 V vs. S.H.E.) provides great potential for building a high-voltage RMBs based on the Mg anode; (iii) Mg element is abundant in the earth's crust, which is important to decrease the production cost; (iiii) The energy densities of Mg are high $(2205 \text{ mAh g}^{-1} \text{ and } 3803 \text{ mAh cm}^{-3})$ [12]. These advantages provide great opportunity for RMBs to be applied in the largescale energy storages.

However, the development of RMBs is still in its early stage and far away from commercialization [13]. The strong polarity of Mg²⁺ resulting from its divalent nature leads to slow diffusion kinetics in solid materials, thus finding suitable cathode materials is one of the greatest challenges in RMBs [14,15]. The most promising cathode material is still Mo₆S₈ proposed by Aurbach group in 2000 [16]. Despite the excellent electrochemical performance for Mg storage, the preparation process of Mo₆S₈ is complex and high energy-consumption, limiting its further application. Although several types of cathode materials are available, their electrochemical performances are not satisfactory. For example, the average discharge voltages of the sulfides, including Mo_6S_8 , are less than 1.5 V vs. Mg^{2+}/Mg , and such low working voltage greatly limits the energy density [16-18]. Developing high-voltage cathode materials is an effective strategy to enhance the energy density. Although several cathode materials based on oxides and polyanions materials with high working voltage have been developed, two challenges still exist at least: (i) The electrochemical performances at RT need further improvement since low current density and high working temperature are usually necessary; (ii) The average discharge voltages are usually much lower than 2.5 V vs. Mg²⁺/Mg [19–24]. Here, the average discharge voltage represents the voltage when the battery reaches half value of the total specific capacity. For instance, it was reported that the MgFeSiO₄ delivered an average discharge voltage of 2 V vs. Mg^{2+}/Mg with a discharge capacity of about 300 mAh g⁻¹ at 55 °C. However, the discharge current density was only $6.62 \,\mathrm{mAg}^{-1}$ $(\sim 0.02 \text{ C})$ and the cycle performance was not provided [19]. Thus, exploration of new cathode materials with high working voltage is highly needed.

The NASICON structured NVP allows fast transportation of Na⁺ due to the opened three-dimensions framework [25]. The NVP delivers a flat plateau at 3.34 V vs. Na⁺/Na with excellent electrochemical performance in SIBs. The theoretical specific capacity is 118 mAh g^{-1} when consider the redox reaction of V⁴⁺/V³⁺. Due to the fast Na⁺

migration ability, the framework of the NVP might also be suitable for the Mg²⁺ transportation. In addition, vanadium-based materials possess good electrochemical performance as electrode materials for both LIBs and RMBs [26-28]. The applications of NVP have first been reported as the cathode material in Na-Mg hybrid batteries. Yao et al. reported a high-voltage rechargeable Na-Mg hybrid battery based on NVP cathode, Mg anode and chlorine-containing electrolyte. However, the insertion of Mg²⁺ into NVP seems difficult due to the incompatibility of the cathode and the electrolyte [29]. By changing the electrolvte to a chlorine-free electrolyte Mg(TFSI)₂/DME, $(TFSI^{-} = C_2F_6NO_4S_2, DME = 1,2$ -dimethoxyethane), Tirado et al. proved the NVP structure is possible for Mg storage with a relatively low discharge voltage of 1.2 V vs. Mg²⁺/Mg. Very recently, we have first investigated the electrochemical performance of the NVP in RMBs with the electrochemically desodiated NVP/C (ED-NVP/C) as the cathode. Despite the high discharge voltage, the insights into the Mg storage mechanism is still not very clear, such as the crystal structure of the Mg²⁺-inserted product. Thus, further investigation is necessary [30].

On the other hand, since NVP shows poor electronic conductivity, the effective structure design and carbon coating process are usually needed [31,32]. The more rational structure design with faster electronic and ionic path can effectively improve the electrochemical performance. The NVP/carbon (NVP/C) composites with honeycomb-like structure can significantly enhance the electrochemical performance of the electrode materials with poor electronic conductivity. This structure with interconnected pores can enlarge the electrode/electrolyte contact area, shorten ion transportation path, as well as accommodate the volume change of the materials [33-35]. Although honeycomb-like porous NVP/C microballs have been synthesized with cetyltrimethylammonium bromide (CTAB) as a soft template, the preparation process is rather complicated and not suitable for mass production [36]. Thus, a convenient and universal method is desired. The spravdrying method is a good choice to integrate inorganic materials with various carbon materials to serve as the electrode materials [28,33,37].

In this work, we have prepared honeycomb-like structured NVP/C/G microspheres by a universal spray-drying method with the polystyrene (PS) as a hard template and the graphene oxide (GO) as the structure support (Fig. 1a). The electrochemical performance of the ED-NVP/C/G for Mg storage is investigated in highly anhydrous electrolyte. The Mg storage mechanism in the ED-NVP/C/G is further studied by the X-ray powder diffraction (XRD), galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectrum (EIS). Finally, a Mg full cell prototype based on the ED-NVP/C/G cathode, Mg metal anode and the electrolyte composed of 0.1 M Mg (TFSI)₂/triglyme is proposed.

2. Experiment

2.1. Preparation of the PS

The PS was synthesized according to the previous report [33]. Typically, styrene (Aladdin) was washed with 4 M NaOH solution to remove the anti-polymerizer before polymerization reaction. The styrene was then washed with deionized water until pH \sim 7. Next, the sodium lauryl (SDS, 0.152 g) and potassium persulfate (KPS, 0.305 g) were added into 140 mL alcohol-water solution (2: 5, volume: volume) in a 250 mL three-neck flask. The polymerization reaction proceeded with the protection of N₂. The solution was heated to 70 °C, and then 7.0 mL of the styrene was added. The solution was kept at 70 °C for 10 h under vigorous stirring. Finally, the as-prepared PS suspension was obtained.

2.2. Preparation of the honeycomb-like structured NVP/C/G

In a typical experiment, the CH_3COONa (0.005 mol, 0.41 g), NH_4VO_3 (0.003 mol, 0.39 g), $NH_4H_2PO_4$ (0.005 mol, 0.552 g) and 0.3 g



Fig. 1. (a) The preparation process of the NVP/C/G; (b-c) SEM images and (d) TEM image of the NVP/C/G; (e-g) High resolution TEM (HRTEM) images for the enlarge areas in (d); (h) XRD patterns and (i) Raman spectra of the NVP/C/G and PNVP; (j) Pore-size distribution of the NVP/C/G.

sucrose were added into 40 mL deionized water. The suspension was kept at 70 °C for 30 min under stirring to dissolve NH_4VO_3 . Then 20 mL PS suspension and 4.0 g GO suspension (0.2 wt%) were added into the transparent yellow solution. The obtained suspension was then under ultrasonic treatment for 1 h. The homogeneous suspension was dried by using a mini spray dryer under the protection of N_2 . The inlet and outlet temperature were 200 °C and 112 °C, respectively. The collected precursors were calcined at 350 °C for 4 h followed by 750 °C for 8 h in 5 wt % H₂/Ar atmosphere to obtain the NVP/C/G. For pure NVP (PNVP), NVP/C and NVP/C-PS, the prepare processes were the same as that of the NVP/C/G without the addition of corresponding reactants.

2.3. Physical characterizations

The XRD measurement was operated on Rigaku Ultima IV or Rigaku miniflex 600 diffractometer. The scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscope (TEM, JEM- 2100) were used to analyze the morphology and crystal nature. The Raman spectra were obtained on the Raman spectroscope (HORIBA Xplora). The thermogravimetric (TG, SDT-Q600) was used to determine the carbon content. The specific surface area was calculated according to the nitrogen adsorption and desorption isotherms (Micromeritics surface area and porosity analyzer, ASAP 2020).

2.4. Electrochemical measurements

The working electrode composes 80 wt% of the NVP/C/G, 10 wt% of the acetylene black and 10 wt% of the polyvinylidene fluoride (PVDF) on Ti foil. The mass loading of the NVP/C/G was 0.6–0.8 mg cm⁻² for electrochemical measurement and ~2.0 mg cm⁻² for ex-situ XRD test. The activated carbon (AC) electrode composes of 80 wt% AC, 10 wt% acetylene black and 10 wt% PVDF on a nickel foam. The mass loading of the AC was ~55 mg cm⁻². For anhydrous electrolyte, the Mg(TFSI)₂·6H₂O (Alfa Aesar) was dehydrated at 200 °C,

and then dissolved in anhydrous acetonitrile (AN, Alfa Aesar). The electrolyte was further dried using molecular sieve for several times. The water content was less than 20 ppm tested by Metrohm 831 Coulometric Karl Fischer titrator. The electrodes were charged to 0.6 V vs. AC in the home-made Swagelok cell to extract two Na from the NVP, and then dissembled in glove box. Anhydrous AN was used to wash the desodiated electrodes several times to remove the residue electrolyte. Then, the half-cell was reassembled with the desodiated electrode as a cathode and the AC electrode as a counter electrode with fresh electrolyte in a 2032-type coin cell.

The galvanostatic charge-discharge test was operated in -0.4 to 0.6 V vs. AC at 0.1 C and 0.2 C (1 C = 100 mAh g⁻¹, considering the carbon materials in the NVP/C/G). For the GITT test, the half-cell was discharged/charged at 0.1 C for 10 min and then relaxed for 1 h. For the EIS test, the cell at different charged/discharged states was tested on the Solartron Modulab 1287A/1260 in 10^{-2} – 10^{5} Hz and the result was confirmed in repeated measurements. The full cell was assembled with the desodiated electrode as a cathode, the metal Mg as an anode and the 0.1 M Mg(TFSI)₂/triglyme (battery grade) as an electrolyte. The stripping/deposition potential of the electrolyte was tested in a Mg//Mg symmetric cells at 1 mA cm^{-2} . The electrochemical performance of the full cell was tested both at RT (25 °C) and high temperature (100 °C) at 0.05 C. For XRD test, to obtain enough intensities to do the XRD refinement, the amount of the active material should be no less than 10 mg. Since the active material loading of NVP/C/G for XRD test is \sim 2.0 mg cm⁻², thus we used six cells for one XRD sample. The cells after desodiation (ED-NVP/C/G) or magnesiation (ED-NVP/C/G-Mg) were dissembled in the glove box and washed with anhydrous AN. After dried at RT, the electrode materials on Ti films were carefully scrape off and collected as one XRD sample. To prevent the influence of air and H₂O, the XRD sample were protected with kapton film before taken out of the glove box.

3. Results and discussion

3.1. Physical characterizations of the NVP/C/G

Fig. 1a presents the preparation process of the NVP/C/G. The droplets containing solvents and solutes are formed through the spray process. Then the solvent at the outside of the droplets will evaporate quickly due to the high temperature, resulting in the formation of a shell contains solutes. Next, the solvent will gradually evaporate from the shell to the inside of the droplets. Finally, after the evaporation, the precursors with hollow structure are obtained. The final product NVP/ C/G is obtained after the calcining process. Here, the sucrose serves as a carbon source. The hard template PS with a diameter of 200 nm (Fig. S2a) acts as an effective macropore-forming agent, since it can completely decompose to gases without residue (Fig. S2b). The rGO sheets in the hollow sphere not only can improve the electronic conductivities, but also play an important role to support the macroporous structure.

The SEM and TEM are employed to study the morphology. The NVP/C/G presents honeycomb-like spheres with particle size from $0.5 \,\mu\text{m}$ to $8 \,\mu\text{m}$, and pores around 100 nm are homogeneously distributed in the NVP/C/G spheres (Fig. 1b–c and Fig. S3a). The hollow structure can be seen from some broken spheres (Fig. S3b). The TEM results (Fig. 1d and Fig. S3c–d) confirm the hollow spheres of the NVP/C/G spheres with macroporous structure. The interplanar distance (Fig. 1e–f) of the NVP/C/G particles is measured to be 0.285 nm and 0.632 nm for area 1 and area 2 in Fig. 1d, corresponding to the d-spacing of (211) and (012) planes of the rhombohedral NVP, respectively. The marked curving lattice fringes (Fig. 1g) in area 3 correspond to the (100) plane of the rGO, confirming the existence of the rGO in the NVP/C/G spheres.

The XRD patterns of the NVP/C/G and PNVP are displayed in Fig. 1h. The results can be well matched with the NVP phase (PDF no. 0053-0018), indicating that the pure phase NVP in both samples are

obtained. The Raman spectra results (Fig. 1i) confirm the existence of C in the NVP/C/G. For PNVP, only typical bands corresponding to the Raman footprints of NVP can be seen [38]. Conversely for the NVP/C/ G, the bands for NVP disappear and two typical bands (D-band and Gband) for carbon materials exist. The intensity ratio of G-band (graphite band) to D-band (disorder-induced phonon mode) is 1.09, revealing that the mixed carbon materials in the NVP/C/G shows overall order phase. The TG analysis result (Fig. S4b-c) shows that the total carbon content in the NVP/C/G is 14.9%. The nitrogen adsorption and desorption isotherms of the NVP/C/G (Fig. S4d) show a type IV curve with the specific surface area of $84.8 \text{ m}^2 \text{ g}^{-1}$. Mesopore in the range of 10 nm-36 nm can be obtained from the pore size distribution (Fig. 1j). The above analyses confirm that the honevcomb-like structured NVP/ C/G has been successfully prepared. The preparation process is facile, controllable and reproducible, indicating that the spray drying method is a good choice to synthesize electrode materials.

3.2. Electrochemical performances of the half-cell

The electrochemical performance of the NVP/C/G has first been evaluated in the SIBs (Figs. S4a, S5). As shown, the NVP/C/G shows better electrochemical performance than the NVP/C-PS and NVP/C, indicating that the honeycomb-like structured design is effective for enhancing the electrochemical performance. Thus, the NVP/C/G is selected as the Mg storage host for further study. To create vacant sites for Mg²⁺ intercalation, the NVP/C/G electrode was first electrochemically desodiated two Na⁺ to get the ED-NVP/C/G. The specific capacity is 97 mAh g^{-1} , corresponding to 1.94 Na⁺ extraction (Fig. S6). Thus, the chemical composition of the ED-NVP/C/G is Na_{1.06}V₂(PO₄)₃. The electrochemical performance of the ED-NVP/C/G has been investigated in a half-cell (Fig. 2a). The AC counter electrode can act as a quasireference electrode in the AN-based solution with a potential of 2.45 V vs. Mg²⁺/Mg [39]. During the charge/discharge process, the Mg²⁺ cations extract from/insert into the ED-NVP/C/G while TFSI- anions desorb from/adsorb on the AC [21,40]. The Fig. 2b presents the voltage profiles of the ED-NVP/C/G at 0.1 C. The ED-NVP/C/G delivers a specific capacity of 87 mAh g^{-1} with an average discharge voltage of 2.47 V vs. Mg²⁺/Mg at the first cycle. A higher average discharge voltage of 2.50 V vs. Mg²⁺/Mg is obtained at the 2nd cycle, which might result from the infiltration of the electrolyte into the porous structure. At 0.2 C, the initial discharge capacity is 78 mAh g^{-1} , and can be remained at 66 mAh g^{-1} at the 50th cycle, corresponding to a capacity retention of 85%. The electrochemical performances can be obtained in the repeated tests. The ED-NVP/C/G shows improved electrochemical performance than the NVP/C without honeycomb structure (Fig. 2c), indicating the rational structure design is also effective in the RMBs. Compared to the developed high-voltage cathode materials, the ED-NVP/C/G delivers higher working voltage and better electrochemical performance at RT than most of the cathode materials. By analyzing the dQ/dV curves (Fig. 2d), it is interesting to find that the curves of the 0.1 C and 0.2 C both present a wider cathodic peak during the discharge process. When the current density increases from 0.1 C to 0.2 C, the cathodic peak become much wider. This phenomenon reveals that the electrochemical reaction is slower during the discharge process, and the Mg²⁺ insertion process is more sensitive to the applied current density. To find the reason, the structure evolution of NVP after desodiation (ED-NVP/C/G) and magnesiation process (ED-NVP/C/G-Mg) have been first investigated.

3.3. Mechanism investigation

The Rietveld refinement results of the XRD patterns of the NVP/C/G, ED-NVP/C/G and ED-NVP/C/G-Mg are shown in Fig. 3a–c. The reliability factors are displayed as follows: for the NVP/C/G, Rp = 4.55% and Rwp = 5.93%; for the ED-NVP/C/G, Rp = 6.55% and Rwp = 7.99%; and for the ED-NVP/C/G-Mg, Rp = 5.44% and



Fig. 2. (a) Illustration of the half-cell; (b) Galvanostatic charge-discharge curves of the ED-NVP/C/G in anhydrous electrolyte at 0.1 C; (c) Cycle performance of the ED-NVP/C/G and ED-NVP/C at 0.2 C; (d) Comparison of the dQ/dV curves of the ED-NVP/C/G at 0.1 C and 0.2 C (the 2nd cycle).

Rwp = 7.21%. The detailed crystallographic data are shown in Table 1 and Tables S1-S3. For the original NVP/C/G, two types of Na atoms, namely the Na1 at 6b sites and the Na2 at 18e site, exist. The occupancies for Na1 and Na2 are 0.80 and 0.74, respectively, corresponding to the chemical composition of Na_{3.02}V₂(PO₄)₃. After desodiation, the occupancy for Na2 decreases to almost zero while the value for Na1 increases to 0.98, thus the chemical composition of the ED-NVP/C/G is Na_{0.98}V₂(PO₄)₃, which is consistent with Na_{1.06}V₂(PO₄)₃ calculated from the charge capacity. This indicates that only about two Na2 can be extracted from the 18e sites and the residue Na2 atoms will migrate to the 6b sites. The variation of the lattice parameters and crystal volume are presented in Fig. 3d. During the Na extraction process, both the a and c axis shrink. The cell volume decreases from 1440.864 to 1327.48 Å³, indicating a small volume change (7.9%) for the NASICON structure [41]. During the following Mg^{2+} insertion process, the 18e sites are gradually occupied by Mg while Na at 6b sites tends to be immobile. The occupancy for Mg is 0.25 after discharged, corresponding to the chemical composition of Mg_{0.75}Na_{0.98}V₂(PO₄)₃. The insertion of Mg^{2+} causes the recovery of the a and c axis, and the cell volume expands to 1410.31 Å³, indicating a volume change of 6.2% with 0.75 Mg²⁺ intercalation. Illustration of the electrochemical reaction process is shown in Fig. 3e. Therefore, the electrochemical reaction based on the XRD results can be written as:

$$Na_{3.02}V_2(PO_4)_3 - 2.04 Na^+ - 2.04 e^- \rightarrow Na_{0.98}V_2(PO_4)_3$$
 (1)

$$Na_{0.98}V_2(PO_4)_3 + 0.75 Mg^{2+} + 1.5e^- \rightarrow Mg_{0.75}Na_{0.98}V_2(PO_4)_3$$
 (2)

The GITT is used to study the diffusion kinetics of Mg^{2+} in ED-NVP/ C/G [17,42,43]. Fig. 4a presents the GITT voltage profiles of the ED-NVP/C/G with the corresponding quasi open-circuit potential (QOCP). For the QOCP curves, only one flat plateau for both processes can be seen, which is induced by the redox reaction of V^{3+}/V^{4+} . The discharge capacity is 96 mAh g⁻¹ with an average discharge voltage of 2.58 V vs. Mg^{2+}/Mg , corresponding to the intercalation of 0.96 Mg^{2+} into each $NaV_2(PO_4)_3$. The calculation of the diffusion coefficient

D_{Mg2+} is based on Fick's second law of diffusion (equation S1) and detailed information is listed in the supporting information. The linear relationship between the E and $\tau^{1/2}$ (Fig. 4b) validates the applicability of the simplified Fick's second law (equation S2). The calculated D_{Mg2+} for the charge and discharge process are displayed in Fig. 4c-d. For both the magnesiation/demagnesiation process, the D_{Mg2+} presents a V-type variation tendency as a function of voltage, which is highly match with the corresponding dQ/dV curves except the region after magnesiation/demagnesiation process. The ED-NVP/C/G exhibits minimum $D_{Mg2\,+}$ at discharge/charge plateau, indicating a two-phase transition mechanism as reported for the LiFePO₄ (LFP) [44,45]. Since Mg²⁺ diffusion occurs within each phase and also through the phase boundary, the measured $D_{\mathrm{Mg2+}}$ is the average value of the diffusion coefficient, namely the apparent diffusion coefficient. The D_{Mg2+} ranges from 1.90×10^{-11} to $1.02 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for the magnesiated process and 2.45×10^{-11} to 4.79×10^{-13} cm² s⁻¹ for the demagnesiation process, respectively. The minimum value for the charge process is about 4 times larger than that of the discharge process, indicating faster Mg²⁺ diffusion during the demagnesiation, which are well match with the phenomenon that the discharge process is more sensitive to the applied current density. Similar phenomenon has also been observed in our previous work [30].

The Nyquist plots of the ED-NVP/C/G at different charge-discharge states (Fig. 4e) are shown in Fig. 4f. Most of the states show a similar Nyquist plots with two semicircles except state H which has a large semicircle at low-middle frequency. An intercept at the Z' axis at high frequency region R_s represents the overall resistance from the electrolyte, separator and electrodes. The semicircle at high frequency corresponds to the resistance (R_{sei}) and capacitance (QPE1) of the solid electrolyte interface (SEI). The semicircle at middle frequency represents the charge transfer resistance (R_{ct}) with its relative double-layer capacitance QPE2 and QPE3 [46,47]. The fitting curves and fitting results of each Nyquist plot are shown in Fig. S7 and Fig. 4g, respectively. The values of the R_s and R_{sei} at state A are 6.4 Ω and 10.9 Ω , respectively, and almost do not change during the charge–discharge



Fig. 3. Rietveld refinement of the XRD patterns of the (a) NVP/C/G, (b) ED-NVP/C/G and (c) ED-NVP/C/G-Mg; (d) Variation of the corresponding lattice parameters (a and c axis) and crystal volume; (e) Illustration of the electrochemical reaction process. Note that the color part of the Na1, Na2 and Mg element represents the occupancy at the corresponding sites.

Table 1

Crystallographic data of the NVP/C/G after desodiation (ED-NVP/C/G) and following magnesiation process (ED-NVP/C/G-Mg).

Atoms	Na1	Na2	Mg	v	Р	01	02
Wyckoff Multicity Occupancy of the NVP/C/G Occupancy of the ED-NVP/C/G Occupancy of the ED-NVP/C/G- Mg	6b 6 0.80 0.98 0.98	18e 18 0.74 0.00 0.00	18e 18 0.00 0.00 0.25	12c 12 1.00 1.00 1.00	18e 18 1.00 1.00 1.00	36f 36 1.00 1.00 1.00	36f 36 1.00 1.00 1.00

process. The R_{ct}, however, decreases from 317Ω to 57Ω during the magnisiation process, and then rapidly increases during the demagnesiation process. The highest R_{ct} (780 Ω) is obtained at the fully charged state with NaV₂(PO₄)₃ as major phase. Considering the variation of the R_{ct} and electrochemical reaction mechanism, it is worth noting that the increase of the R_{ct} is positively related to the formation of the NaV₂(PO₄)₃ phase. This variation can be confirmed by repeated measurements. Similar phenomenon has also been found in the LFP [47]. Based on the XRD, GITT and EIS analyses, the Mg storage mechanism in

the ED-NVP is very similar to that of the Li in FePO₄.

3.4. The electrochemical performances of the Mg full cell

The main purpose for developing high-voltage cathode materials is to combine metal Mg as an anode and build the Mg full cell with high energy density. Unfortunately, the electrochemical performances of the high-voltage cathode materials are usually tested in a three-electrode system and only a few Mg full cells have been reported. Here, we build a Mg full cell prototype using the ED-NVP/C/G electrode as a cathode and Mg metal as an anode in 0.1 M Mg(TFSI)₂/triglyme (Fig. 5a). The onset potential of the electrolyte for Mg stripping/deposition has been measured using a Mg//Mg symmetric cell at 1 mA cm^{-2} . The initial Mg stripping/deposition process exhibits a large overpotential up to 2.5 V vs. Mg^{2+}/Mg (Fig. 5b). The large voltage polarization results from native passive layer on Mg anode with the passive layer caused by the reaction of Mg metal with Mg(TFSI)₂ [48]. At the second cycle, the overpotential decreases to 0.33 V vs. Mg²⁺/Mg and becomes stable in the following few cycles. The full cell shows a rather low discharge voltage of 0.6 V vs. Mg^{2+}/Mg and a low specific capacity of 12 mAh g^{-1} at RT (Fig. S8). The EIS results (Fig. S9) reveal that the



Fig. 4. (a) GITT curves of the ED-NVP/C/G; (b) Transient voltage of the galvanostatic pulse (E) as a function of the square root of time ($\tau^{1/2}$) for the ED-NVP/C/G; D_{Mg2+} for the ED-NVP/C/G electrode as a function of cell voltage during both (c) discharge and (d) charge processes with the corresponding dQ/dV curves calculated from the QOCP curves; (e) Voltage profiles of the ED-NVP/C/G at different charge-discharge state and (f) corresponding Nyquist plots; (g) Variation tendency of the R_{ctb} R_{sei} and R_s.

А

change of the solvent from AN to triglyme leads to a little higher R_{ct}, which might result from the higher desolvation energy of Mg^{2+} from Mg²⁺-triglyme complex [49,50]. The high viscosity nature of the triglyme might be responsible for the increased R_s. However, the main reason is the large R_{sei} (~10⁴ Ω) from the Mg anode (Fig. 5d). To improve the reaction kinetics, the electrochemical performance of the full cell has been further measured at high temperature (100 °C). An initial discharge capacity of 80 mAh g^{-1} with an average discharge voltage of 1.3 V vs. Mg^{2+}/Mg is obtained (Fig. S10). At the second cycle, the specific capacity increases to 92 mAh g⁻¹ with a higher discharge voltage of 1.5 V vs. Mg²⁺/Mg (Fig. 5c) due to the smaller overpotential for Mg dissolution from Mg anode. Compared the Nyquist plots of the full cell at RT with that at 100 °C, it is obvious that the high temperature can lower the R_{sei} from $\sim\!10^4~\Omega$ to $\sim\!10^3~\Omega.$ However, a much larger R_{sei} still exists compared to the half-cell (Fig. S9), leading to a poorer electrochemical performance. Due to the large R_{sei}, it is difficult for the full cell to work well. In addition, the high working temperature causes the ethers to decompose at ~ 2.5 V vs. Mg²⁺/Mg. The result indicates that more suitable electrolyte that are compatible to both cathode and Mg anode are highly needed for Mg full cells. The reaction mechanism of the full cell during discharge process can be written as:

Cathode:
$$Na_{0.98}V_2(PO_4)_3 + 0.92 Mg^{2+} + 1.84 e^- \rightarrow Mg_{0.92}Na_{0.98}V_2(PO_4)_3$$

$$anode: Mg - 2e^- \to Mg^{2+} \tag{6}$$

Overall reaction: $Na_{0.98}V_2(PO_4)_3 + 0.92 Mg \rightarrow Mg_{0.92}Na_{0.98}V_2(PO_4)_3$

Compared to the reported high-voltage cathode materials composed of polyanion materials and oxides (Table S4), the developed ED-NVP/ C/G not only delivers relatively high working voltage at higher current densities (0.2 C), but also can match with Mg metal anode as a full cell with better electrochemical performance.

4. Conclusion

In this work, we have successfully prepared honeycomb-like



Fig. 5. (a) Illustration of the full cell; (b) Voltage profiles of the Mg//Mg symmetric cell in $0.1 \text{ M} \text{ Mg}(\text{TFSI})_2/\text{triglyme at } 1 \text{ mA cm}^{-2}$; (c) Voltage profiles of the ED-NVP/C/G in the full cell at 2nd cycle (0.05 C, 100 °C); (d) Nyquist plots of the full cell at RT and 100 °C at OCV.

structured NVP/C/G via a convenient and universal spray-drying method with improved electrochemical performance. An initial capacity of 87 mAh g^{-1} and an average discharge voltage of 2.47 V vs. Mg^{2+}/Mg are obtained in highly anhydrous electrolyte at 0.1 C. The investigation of the Mg storage mechanism shows that the cell unit of the ED-NVP expands during the magnesiation process, and the inserted Mg²⁺ tends to occupy the Na2 vacant sites in the NVP crystal structure. The electrochemical reaction takes place via a two-phase transition with larger $D_{M\sigma^2+}$ in the demagnesiation process, indicating that the Mg extraction kinetics is faster. The Rct of the half-cell varies at different charge-discharge states and shows a positive relationship to the formation of NaV₂(PO₄)₃ phase. The Mg storage mechanism in the ED-NVP is very similar to that of Li in FePO₄. The Mg full cell prototype based on the ED-NVP/C/G cathode and Mg metal anode is proposed. The electrochemical performance of the full cell is much poorer than the half-cell, indicating that a more suitable chlorine-free electrolyte that are compatible to both cathode and Mg anode is highly needed. In conclusion, the rational structure design improves the electrochemical performance for Mg storage, and our work also gives new understanding into the Mg storage mechanism in the ED-NVP structure.

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Conflict of interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.04.128.

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