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An Insight into the Electrochemical Activity of Al-doped V_2O_3

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We design Al-doped V_2O_3 ($Al_xV_2O_3$) compounds as cathodes of aluminium battery. A citric acid-assisted simple solid-state synthesis is used to produce $Al_xV_2O_3$ compounds by heating, at different temperature, a reaction mixture of NH_4VO_3 , $Al(NO_3)_3 \cdot 9H_2O$ and citric acid under Ar flow. Al-doping in-between layers and at lattice sites of V_2O_3 is confirmed by structural, vibrational and chemical analyses. The doped compounds obtained at 600 °C and 800 °C are confirmed as $Al_{0.56}V_2O_3$ and $Al_{0.53}V_2O_3$ corresponding to theoretical capacities 488 and 490 mAh g⁻¹, respectively, for the extraction of doped Al by considering three electron transfer (Al/Al^{3+}). The as-synthesized $Al_xV_2O_3$ compounds are tested as cathodes in aluminium battery with 1.0 M $AlCl_3$:[EMIM]Cl electrolyte. The electrodes of $Al_{0.56}V_2O_3$ and $Al_{0.53}V_2O_3$ exhibited the first charge capacity of 415 and 385 mAh g⁻¹, respectively. The electrochemical extraction of doped Al is confirmed by comparisons with bare V_2O_3 control cathodes and post-cycling structural studies. The extraction of doped Al from $Al_xV_2O_3$ indicates its promising use in high capacity cathode for Al-ion battery.

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In this advanced technological era, lithium-ion based battery has been extensively used for electrochemical storage to power the ever-growing portable devices and mobile applications due to its superior power and energy densities.¹⁻⁴ This leads to a growing concern on the high cost and availability of lithium in the reserves of Earth's crust to meet the future demands.¹⁻³ Therefore, there is a need to shift towards alternative metal-ions (e.g., Na^+ , Mg^{2+} , Al^{3+} etc.) for a greener, sustainable and large-scale electrochemical energy storage system.⁵⁻¹⁶ However, due to the larger ionic sizes and higher redox potential of the aforementioned metal-ions, their power and energy densities are inferior as compared to the ones of lithium-ion.^{5,6,17} Therefore, significant research efforts have been devoted to improve the power and energy densities in these alternative metal-ions energy storage system via structural modification,^{9,10,14} doping,^{7,10} coating of electrode materials⁸ as well as electrolytes design^{13,15} and optimization.

Among the energy storage systems based on the alternative metal-ions, rechargeable aluminum-based batteries (ABs) are extremely promising due to the Al abundance and high volumetric capacity (i.e., 8.04 A h cm⁻³).^{12,18-25} In the quest to design high energy density storage devices, the selection of host materials with high theoretical capacities is key.^{11,12} Recent developments of ABs have been focused on vanadium-based oxides, V_2O_5 , due to its potentially high theoretical capacity of 442 mA h g⁻¹ enabled by the insertion of Al^{3+} ion.²⁶⁻²⁸ However, vanadium (III) oxide (V_2O_3) has been previously reported as an alternative high capacity material for Li, Na and K-ion storage.²⁹⁻³⁴ In the context of ABs, V_2O_3 is an attractive cathode material that can potentially achieve an even higher theoretical capacity i.e., 536 mA h g⁻¹ compared to the one of V_2O_5 (442 mA h g⁻¹).²⁶⁻²⁸

To the best of our knowledge, V_2O_3 has yet to be investigated as cathode material for ABs. Herein, we report a novel Al-doped V_2O_3 ($Al_xV_2O_3$) cathode material synthesized at two different temperatures via a facile one-pot citric acid (CA , $C_6H_8O_7$) assisted solid-state process by using ammonium metavanadate (NH_4VO_3) and aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$).²⁹ NH_4VO_3 is insoluble in water and efforts to make it soluble lead to the formation of long polyvanadate chains of VO_3^- that contain corner shared VO_4

tetrahedra.³⁵ Such a polyvanadate phase often leads to the formation of V_2O_5 upon heat treated.³⁶ Citric acid can inhibit the polyvanadate chains by forming "ammonium dimeric vanadium (V) citrate complex," $(NH_4)_2[VO_2(C_6H_6O_7)_2]$.^{37,38} Citric acid not only inhibits the polyvanadate chains but also dissolves the NH_4VO_3 .^{37,38} The resultant reaction mixture does not favours further polymerization of citrate complex to produce gel network, which is a key factor in controlling the particle size, contrarily to the typical CA sol-gel method.³⁹ In general, low dimensional materials have several advantages for energy storage application.¹⁶ Due to lack of gel formation, large particulates ($\sim 1-100 \mu m$) of crystalline V_2O_3 phase was obtained in our recent study.²⁹ The same method is adapted to synthesize $Al_xV_2O_3$ by adding $Al(NO_3)_3 \cdot 9H_2O$ as Al-precursor and changing the reaction temperature. Two sets of the doped compounds, along with their bare counterparts, are prepared at 600 °C and 800 °C. Thus, prepared $Al_xV_2O_3$ and V_2O_3 compounds are characterized for their physical and chemical properties and eventually tested for their suitability as cathodes of AB pouches with 1.0 M $AlCl_3$:[EMIM]Cl electrolyte. The $Al_xV_2O_3$ cathodes exhibited characteristics for extraction of doped Al during the first charge with corresponding capacities within the range of theoretical predictions, whilst bare V_2O_3 compounds exhibited tetrachloroaluminate anion ($AlCl_4^-$) insertion characteristics only. The post-cycling structural studies of both bare and Al doped V_2O_3 compounds confirmed the electrochemical extraction of dopant Al.

Experimental

Aluminium-doped and bare V_2O_3 compounds were synthesized by simple CA assisted solid-state approach. $Al_xV_2O_3$ powder samples were prepared by heating solid reaction mixture containing $Al(NO_3)_3 \cdot 9H_2O$, NH_4VO_3 and CA under Ar flow at 600 °C and 800 °C for 10 h. The reaction mixture is prepared by dissolving 0.01 moles of $Al(NO_3)_3 \cdot 9H_2O$ and 0.01 moles NH_4VO_3 in 25 ml of 0.3 M CA aqueous solution, heated at 100 °C overnight to obtain dry powder. The bare V_2O_3 powders were prepared, under same conditions, as control samples. Thus, synthesized compounds were named as $Al_xV_2O_3@600^\circ C$, $V_2O_3@600^\circ C$, $Al_xV_2O_3@800^\circ C$ and $V_2O_3@800^\circ C$. X-Ray Diffraction (XRD) studies in the range of 20°–80° were carried out with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) using Bruker D8 Advance. The physical morphology and elemental

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distribution of the samples was analysed using JEOL JSM-7600F Field Emission Scanning Electron Microscopy (FESEM). Inductively coupled plasma optical emission spectrometry (ICP-OES) testing was performed using Agilent 720 with a detection limit of 0.02 ppm. 3jX-ray photoelectron spectroscopy (XPS) measurements were performed with 250 W Al K α beam source and a position-sensitive detector (PSD) using PHI-5400 equipment. High-resolution survey spectra were analyzed with the Casa XPS software package. Raman spectroscopy was carried out with an excitation wavelength of 488 nm using confocal Raman WITec set up. The post-cycling ex situ XRD analysis in the range of 20°–60° was performed on a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu K α ceramic X-ray tube.

The electrodes of four compounds on Mo substrate (2.0 × 1.5 cm²) were prepared by drop casting an electrode slurry of as-synthesized powders, polyvinylidene fluoride (PVDF) and super P carbon (SPC) in 80:10:10 wt%, respectively. Pouch cells of the electrodes were fabricated inside an Ar-filled glove box with high purity Al metal foil (99.999%, Sigma Aldrich) as a counter electrode, glass microfiber filter paper (GF/F, Whatman Int. Ltd.) as separator and 1.0 M of AlCl₃ in 1-ethyl-3 methyl imidazolium chloride ([EMIM]Cl) ionic liquid (IL) as electrolyte. To make the AB pouches, aluminium laminated films (MTI) used as casing and customized Mo tabs used as current collectors. The electrodes coated on stainless steel (SS, 16 mm disc) were used to prepare CR2016 coin cells. Thus, fabricated AB pouch and coin cells were tested at room temperature for their performance with a current density of 49 mA g⁻¹ in the voltage window of 0.01–2.45 V using Bio-Logic BCS-805 battery cycling system. The same voltage window and instrument was used to perform cyclic voltammetry (CV) measurements at a scan rate of 0.1 mV s⁻¹. The cells were first charged from open circuit voltage (OCV) to 2.45 V and then subsequently discharged to 0.01 V.

Results and Discussion

The two sets of XRD patterns shown in Fig. 1 confirm the pure V₂O₃ phase formation, if compared to PDF#1-71-342 (space group: R-3c (167)). A sequential increase in the peak intensity and crystallite size (Table I) is detected with both the raise in temperature and Al-doping. In particular, the peaks intensity has been doubled, for the samples synthesized at 600 °C, upon Al doping. Contrarily, the peaks intensity, for the samples synthesized at 800 °C, increased by only ~20%. However, in the latter case, additional peaks at 31.26, 37.19, 57.21, 66.25 and 79.47° are detected. Our data indicate that Al doping increases the crystallinity of V₂O₃ in addition to the effect of the temperature. The lattice parameters of bare V₂O₃ at both the synthesis temperatures are quite

similar, as shown in Table I. An expansion of lattices in *a* and *b*-directions and a contraction in *c*-direction of V₂O₃ is observed upon Al-doping. These changes in lattices are more evident with the temperature treatment, as reported in Table I. The observed changes in the lattice suggests that the Al-doping has the potential to determine distortions in the original structure. These inferences are in agreement with theoretical study reported elsewhere²¹ wherein, it was estimated that Al doping into VO₆ octahedra requires more than two atoms for a significant change in the structure.²¹ In our study, the Al-doping (0.53 < *x* < 0.56) is well below, to avoid distortion of the V₂O₃ native phase. The ionic radii of V³⁺ and Al³⁺ are 0.078 nm and 0.068 nm,⁴⁰ respectively, and V replacement by Al will lead to significant reduction in lattice parameter. Our data, reported in Table I, excludes lattice distortions. Absence of significant changes in the lattice parameters signifies the presence of doped Al in tetrahedral and octahedral sites of V₂O₃ as reported for VO₂.²¹ Further, evolution of new peaks in the pattern of Al_{*x*}V₂O₃@800 °C indicates doping at lattice points i.e., V³⁺ replaced by Al³⁺. However, the weak intensity of these additional peaks suggests a partial substitution of V atoms by dopant Al.

The physical morphology, investigated by FESEM, and the Al and V elemental distribution maps of Al_{*x*}V₂O₃@600 °C and Al_{*x*}V₂O₃@800 °C powders are shown in Figs. 2a–2c and 2d–2f, respectively. For the two samples, the particles have random shapes, with size ranging from submicron to a few tens of microns. The observed particles size is significant reduced compared to their undoped counterparts (see Fig. S1 is available online at stacks.iop.org/JES/167/100514/mmedia). Thus, Al doping has a twofold effect, it reduces the particle size and increases the crystallinity as detected in XRD analysis. The doped Al is rather homogeneously distributed throughout the V₂O₃ phase in both samples, as shown in the corresponding elemental distribution maps (see Fig. 2). Formulae of Al_{*x*}V₂O₃ estimated from ICP are as shown in Table II. The extent of Al doping, i.e., “*x*”, is determined from ICP as 0.56 and 0.53 for Al_{*x*}V₂O₃@600 °C and Al_{*x*}V₂O₃@800 °C, respectively. Thus, determined formulae Al_{0.56}V₂O₃ and Al_{0.53}V₂O₃ corresponds to theoretical capacity of 488 and 490 mAh g⁻¹ for electrochemical extraction of the doped Al by considering three electron transfer (Al/Al³⁺), described in Eq. 1.

To further investigate the chemical composition of the Al doped samples, we used XPS analysis, see Fig. 3. The high resolution V 2p spectra of bare V₂O₃@600 °C and V₂O₃@800 °C (Figs. 3a–3b) are in good agreement with our recent report.²⁹ The binding energy and atomic percentage (At%) of V³⁺ and V²⁺ are shown in Table III. It is common to see a small percentage of V in +2 oxidation state, as seen in other V₂O₃ compounds reported elsewhere.²⁹ After Al doping, the At% of V³⁺ in Al_{*x*}V₂O₃ is reduced, whilst the V²⁺ one is increased instead (Figs. 3d–3e). The At% of V²⁺ in Al_{*x*}V₂O₃ compounds is found exceeding V³⁺ with the increase in temperature, see Table III. The Al in V₂O₃ oxidises (Al → Al³⁺ + 3e⁻) and transfers electrons that reduce V³⁺ to V²⁺. It is not possible to further reduce V²⁺ to V¹⁺ as this oxidation state does not exist.^{41,42} Similar changes in the oxidation states is also noted in an electrochemical insertion of Al³⁺ in V₂O₅ that created V³⁺ and V⁴⁺ oxidation states in addition to the original V⁵⁺ one.⁴³ As shown in Figs. 3c and 3f, and reported in Table III, the position of Al 2p

Table I. Rietveld refinement results of V₂O₃ and Al_{*x*}V₂O₃ XRD patterns.

Sample name	Lattice parameters (Å)	Crystallite size (nm)
V ₂ O ₃ -600 °C	<i>a</i> = 4.960(4); <i>c</i> = 13.993(3)	21.4
Al _{<i>x</i>} V ₂ O ₃ -600 °C	<i>a</i> = 4.974(6); <i>c</i> = 13.995(1)	36.8
V ₂ O ₃ -800 °C	<i>a</i> = 4.960(8); <i>c</i> = 13.989(7)	39.0
Al _{<i>x</i>} V ₂ O ₃ -800 °C	<i>a</i> = 5.010(0); <i>c</i> = 13.941(1)	70.1
PDF#1-71-342	<i>a</i> = 4.9492; <i>c</i> = 13.9980	—

Table II. Elemental analysis of Al_{*x*}V₂O₃ from ICP.

Name	Al _{<i>x</i>} V ₂ O ₃ @600 °C			Al _{<i>x</i>} V ₂ O ₃ @800 °C		
	Weight %	Atomic %	Formula	Weight %	Atomic %	Formula
Al	6.70	21.84	Al _{0.56} V ₂ O ₃	7.17	21.08	Al _{0.53} V ₂ O ₃
V	45.26	78.16		50.68	78.92

Figure 1. XRD patterns of V_2O_5 and $Al_xV_2O_5$ synthesized at 600 °C and 800 °C, and the crystal structure of $V_2O_5@600$ °C.

confirms that dopant Al is in +3 oxidation state,^{44,45} which is in conform with the changes in the vanadium's oxidation states. The XPS results confirm the EDAX and ICP data, validating the formulae estimated for both $Al_xV_2O_5$ compounds.

Raman spectra of the bare and doped V_2O_5 are shown in Fig. 4. These four spectra are found consistent with each other as well as with earlier reports. The main difference between the pristine and doped V_2O_5 is the vanishing of 870 cm^{-1} peaks upon doping. The peak at 870 cm^{-1} in undoped V_2O_5 is due to the formation of amorphous (a)- VO_x phase due to laser degradation.⁴⁶ The doped Al hindered the formation of a- VO_x phase because it has strong affinity to bind with escaping oxygen⁴⁷ upon laser degradation. The oxidation of doped Al weakens the V–O coordination and, in turn, the corresponding vibrations. For the same reason, the intensity of the other peaks reduced significantly in doped samples. Nevertheless, the four compounds have peaks corresponding to oxygen bonded/coordinated to single, double and triple vanadium atoms as shown in Table SI. The peak at $\sim 990\text{ cm}^{-1}$ belongs to

oxygen bonded to vanadium (V=O) at crystal edges.^{29,48} Thus, the Raman analysis is consistent with the XRD, ICP and XPS data.

Aluminium battery characterization.— $Al_{0.53}V_2O_5$ is tested as cathode in a SS304 coin cell. The corresponding charge-discharge characteristics are shown in Fig. 5a. During the first charge, the extraction of the doped Al takes place according to Eq. 1.²² However, the first charge capacity is 627 mAh g^{-1} , a value that exceeds the theoretical one (490 mAh g^{-1}) estimated from ICP data. This additional capacity is linked with irreversible processes, and can be attributed to the corrosion of SS304 casings, see Eqs. 2–3.⁴⁹

During the discharge process it is noted that the potential instantaneously drops to 0.5 V vs Al. We assume at this stage that

Figure 2. FESEM image and corresponding elemental distribution maps of $\text{Al}_x\text{V}_2\text{O}_3$ obtained at (a)–(c) 600 and (d)–(f) 800 °C.

Figure 3. XPS spectra of V 2p in (a) V_2O_3 @600 °C, (b) V_2O_3 @800 °C, (d) $\text{Al}_x\text{V}_2\text{O}_3$ @600 °C, (e) $\text{Al}_x\text{V}_2\text{O}_3$ @800 °C; Al 2p in (c) $\text{Al}_x\text{V}_2\text{O}_3$ @600 °C and (f) $\text{Al}_x\text{V}_2\text{O}_3$ @800 °C.

Table III. XPS analysis of the V_2O_3 and $\text{Al}_x\text{V}_2\text{O}_3$ compounds.

Name	V 2p _{3/2} position (eV)		At% of V 2p _{3/2}		Al 2p position (eV)
	V ³⁺	V ²⁺	V ³⁺	V ²⁺	
V_2O_3 @600 °C	517.60	516.29	74.02	25.98	—
$\text{Al}_x\text{V}_2\text{O}_3$ @600 °C	517.69	516.66	54.12	45.88	74.34
V_2O_3 @800 °C	517.46	516.03	79.68	20.32	—
$\text{Al}_x\text{V}_2\text{O}_3$ @800 °C	517.57	516.44	47.41	52.59	74.66

this effect is due to interfacial impedance on the surface of the electrode. However, a full understanding of this effect requires further experimental work and falls beyond the scope of this work. Apart from

the aforementioned effect, it is also not trivial to de-convolute the contributions of Eqs. 1–3 to the total capacity.⁴⁹ Due to these difficulties, further battery testing is pursued with pouch cells to avoid

Figure 4. Raman spectra of V_2O_3 (green curves) and $\text{Al}_x\text{V}_2\text{O}_3$ (red curves) powders prepared at 600 °C and 800 °C.

any corrosion type reactions that might be occurring with stainless steel. In contrast with the coin cell case, as shown in Fig. 5b, $\text{Al}_{0.53}\text{V}_2\text{O}_3$ as cathode in pouch cell AB exhibits a single charging plateau between 2.0–3.0 V with a specific capacity of 586 mAh g^{-1} as determined by Eq. 1. The additional capacity beyond the theoretical one is, also in this case, linked with irreversible processes and in particular with electrolyte decomposition.⁵⁰ To avoid this unwanted process, we used a potential is cut off set at 2.45 V for further experiments.⁵⁰

The two-stage intercalation of AlCl_4^- during the first charge of $\text{V}_2\text{O}_3@600^\circ\text{C}$ (Fig. 6a) and $\text{V}_2\text{O}_3@800^\circ\text{C}$ (Fig. 6c) is found similar to the one of graphite,^{22,23} corresponding to the total charge capacity of 74 and 113 mAh g^{-1} , respectively. On the contrary, $\text{Al}_{0.56}\text{V}_2\text{O}_3$ (Fig. 6b) and $\text{Al}_{0.53}\text{V}_2\text{O}_3$ (Fig. 6d) exhibited a single charging plateau in the 2.0–2.45 V range, reaching capacities of 415 and 380 mAh g^{-1} , respectively. These values are within the range of respective theoretical capacities for electrochemical extraction of Al

Figure 5 Charge-discharge features of $\text{Al}_x\text{V}_2\text{O}_3@800^\circ\text{C}$ in (a) coin cell and (b) pouch cell.

Figure 6. Voltage-Capacity profiles of (a) V_2O_3 @600 °C, (b) $\text{Al}_x\text{V}_2\text{O}_3$ @600 °C, (c) V_2O_3 @800 °C and (d) $\text{Al}_x\text{V}_2\text{O}_3$ @800 °C.

according to Eq. 1.^{22,23,51,52} In all four cases, the subsequent cycling features have shown continuous capacity decay (Fig. S2) due to structural damage of the V_2O_3 phase as shown in Fig. 7. The reason can be attributed to large ionic sizes of AlCl_4^- (~ 6.09 Å and Al_2Cl_7^- ~ 10.51 Å (estimated from ionic radii of Al^{3+} (0.68 Å) and Cl^- (1.67 Å)).^{40,53} As reported in Fig. 7, the post-cycling XRD patterns confirm both $\text{Al}_x\text{V}_2\text{O}_3$ and V_2O_3 compounds undergoing identical structural changes towards complete amorphization that eventually lead to a- VO_x phase formation.

Insertion of AlCl_4^- and its subsequent reaction with dopant Al to form Al_2Cl_7^- could definitely distort V_2O_3 structure due to their large ionic sizes (greater than inter layer spacing d_{012} ~ 3.66 Å and d_{110} ~ 2.476 Å) that plausibly lead to complete amorphization during cycling. The formation of Al_2Cl_7^- could have created extra space between the layers of $\text{Al}_x\text{V}_2\text{O}_3$ to accommodate more AlCl_4^- ions, which justify the additional capacity. The specific capacity values of pristine and Al-doped V_2O_3 compounds fall within the same range, once the extraction of dopant Al and subsequent amorphization effect nullifies as shown in Fig. S2. This interpretation supports the claim of Eq. 1 as the main reason for the additional capacity reported for the extraction of doped Al. The new a- VO_x phase observed could have easily benefitted in the storage of Li^+ and Na^+ ions as it offer short diffusion paths.^{29,54} Also Al^{3+} ions share the same features of a- VO_x , but in the present case the electrolyte allows only the storage of AlCl_4^- . The larger ionic size of AlCl_4^- compared to Al^{3+} might reduce such advantage, negatively affecting the capacity. The binder PVDF and SPC might have also contributed to the capacity fading as they can interact and decompose the electrolyte (SPC above 2.0 V).^{43,53,55,56}

In fact, as seen in Fig. 7d, the SPC after the first discharge has shown several peaks that might be the result of the interactions

between electrolyte species and carbon atoms that are either graphitic or disordered. The (002) and (100) graphitic domains of SPC as seen in Fig. 7d, such as carbon hexagons in graphite or graphene, result in few peaks corresponding to AlCl_4^- staging phenomenon.^{22,23,53,57,58} Hence, the additional peaks could be ascribed to disordered carbons. Blending nanocomposites of $\text{Al}_x\text{V}_2\text{O}_3$ and V_2O_3 compounds with graphene flakes,¹⁷ as in the case of silicon,^{16,59,60} is expected to improve the stability of these electrodes by stemming off the side reactions previously occurring with SPC. The pouch cell cyclic voltammetry characteristics of V_2O_3 and $\text{Al}_{0.56}\text{V}_2\text{O}_3$ are shown in Fig. 8. During the first charge, there is only one large peak noticed starting from OCV (~1.8 V) to 2.45 V in both cases, corresponding to the intercalation of AlCl_4^- into the electrode matrix.^{22,23,51,52} In the case of $\text{Al}_{0.56}\text{V}_2\text{O}_3$, an increase in current compared V_2O_3 is detected, which is an indication of Al extraction as set by Eq. 1. The peaks detected at ~1.42 and ~2.26 V from the second charge process onwards in both cases belongs to dissociation of Al_2Cl_7^- (to AlCl_4^-) and AlCl_4^- intercalation, respectively.⁵¹ During the first discharge process, the peak at ~1.60 V in both cases is ascribed to de-intercalation of AlCl_4^- ,^{22,23,51,52} which shifted to higher voltages from the second cycle onward. The second peak at ~1.0 V could be associated to electrolyte side reaction(s), for example, reaction with PVDF to form stable compounds such as AlF_3 .^{51,56} These unknown side reaction(s) seem to be irreversible as the corresponding peak diminishes within the first three cycles. However, the remaining peaks also disappear with cycling, from fifth cycle only a weak signal of AlCl_4^- (de) intercalation in-between 1.8–2.45 V can be observed. This could be attributed to the structural destruction as evidenced in post-cycling XRD patterns (Fig. 7). There are no signs of aluminium plating ($\text{Al}^{3+} \rightarrow \text{Al}^0$ @ -2.0 to 0.5 V) and stripping ($\text{Al}^0 \rightarrow \text{Al}^{3+}$ @ 0.0 to

Figure 7. The post-cycling ex situ XRD patterns of (a) $\text{Al}_{0.56}\text{V}_2\text{O}_3$, (b)–(c) V_2O_3 and (d) SPC after first charge (2.45 V; red curves) and first discharge (0.01 V; blue curves) states in comparison to starting powders (black curves).

Figure 8. The cyclic voltammograms of (a) $\text{V}_2\text{O}_3@600\text{ °C}$ and (b) $\text{Al}_{0.56}\text{V}_2\text{O}_3$ recorded at 0.1 mV s^{-1} scan rate.

0.8 V) visualised in both cases throughout the cycles tested.^{52,61,62} The overall CV features observed are in agreement with galvanostatic cycling and post-cycling XRD results. The present pouch cell electrochemistry clarifies that in a typical combination of AlCl_3 -IL electrolyte and vanadium oxide cathodes, the main workhorses of charge storage are AlCl_4^- and Al_2Cl_7^- , and not the reduction of AlCl_3 to Al/Al^{3+} to intercalate into electrode matrix as disconcerted in previous reports.^{21,27,28,49,61} The shift in the charge-discharge potentials of $\text{Al}_x\text{V}_2\text{O}_3$ below 1.5 V inside the coin cell testing appear to be extraction of the doped Al as set in Eq. 1 screened by SS side

reactions according to Eqs. 2 and 3.⁴⁹ This complex electrochemistry of AlCl_3 -IL electrolyte emphasizes urgent need to design a new electrolyte that is free from SS corrosion.

Conclusions

We presented citric acid-assisted solid-state synthesis of $\text{Al}_x\text{V}_2\text{O}_3$ compounds. The extent of Al doping i.e., “x” is determined from the elemental analysis as 0.56 and 0.53 at 600 and 800 °C synthesis temperature, respectively. The presence of the doped Al in V_2O_3 at

polyhedral voids and lattice sites is confirmed with a combination of structural, chemical and Raman analyses. We exploited $\text{Al}_{0.56}\text{V}_2\text{O}_3$ and $\text{Al}_{0.53}\text{V}_2\text{O}_3$ as cathodes in aluminium battery pouches, delivering a first charge specific capacity values of 415 and 385 mAh g^{-1} , respectively. The obtained values are significant higher compared to their control bare V_2O_3 samples, which have reached specific capacities of 74 and 113 mAh g^{-1} , respectively. The subsequent charge/discharge cycling features of both $\text{Al}_x\text{V}_2\text{O}_3$ and V_2O_3 cathodes have shown a continuous specific capacity decay. A possible solution of this issue could be the blending of $\text{Al}_x\text{V}_2\text{O}_3$ and V_2O_3 compounds with graphene flakes that improves the overall conductivity of the composite and buffers the volume changes. The amorphization of both $\text{Al}_x\text{V}_2\text{O}_3$ and V_2O_3 upon the first intercalation/de-intercalation of AlCl_4^- and the subsequent performance degradation recommends designing a new electrolyte that could allow single atomic Al/Al^{3+} insertion and extraction to improve the electrochemical performance.

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References

- J. M. Tarascon and M. Armand, *Materials for Sustainable Energy* (Co-Published with Macmillan Publishers Ltd., United Kingdom) p. 171 (2010).
- B. Dunn, H. Kamath, and J.-M. Tarascon, "Electrical energy storage for the grid: a battery of choices." *Science*, **334**, 928 (2011).
- Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, and J. Liu, "Electrochemical energy storage for green grid." *Chem. Rev.*, **111**, 3577 (2011).
- L. Qiu, W. Xiang, W. Tian, C.-L. Xu, Y.-C. Li, Z.-G. Wu, T.-R. Chen, K. Jia, D. Wang, and F.-R. He, "Polyanion and cation co-doping stabilized Ni-rich Ni-Co-Al material as cathode with enhanced electrochemical performance for Li-ion battery." *Nano Energy*, **63**, 103818 (2019).
- Y. Liang, W. H. Lai, Z. Miao, and S. L. Chou, "Nanocomposite materials for the sodium-ion battery: a review." *Small*, **14**, 1702514 (2018).
- L. Fu, N. Li, Y. Liu, W. Wang, Y. Zhu, and Y. Wu, "Advances of aluminum based energy storage systems." *Chin. J. Chem.*, **35**, 13 (2017).
- R. Chua, Y. Cai, Z. K. Kou, R. Satish, H. Ren, J. J. Chan, L. Zhang, S. A. Morris, J. Bai, and M. Srinivasan, "1.3 V superwide potential window sponsored by Na-Mn-O plates as cathodes towards aqueous rechargeable sodium-ion batteries." *Chem. Eng. J.*, **370**, 742 (2019).
- Y. Wang, C. Wu, Z. Wu, G. Cui, F. Xie, X. Guo, and X. Sun, "FeP nanorod arrays on carbon cloth: a high-performance anode for sodium-ion batteries." *Chem. Commun.*, **54**, 9341 (2018).
- C. Wu, W. Hua, Z. Zhang, B. Zhong, Z. Yang, G. Feng, W. Xiang, Z. Wu, and X. Guo, "Design and synthesis of layered $\text{Na}_2\text{Ti}_3\text{O}_7$ and tunnel $\text{Na}_2\text{Ti}_6\text{O}_{13}$ hybrid structures with enhanced electrochemical behavior for sodium-ion batteries." *Advanced Science*, **5**, 1800519 (2018).
- Y. Xiao, P. F. Wang, Y. X. Yin, Y. F. Zhu, Y. B. Niu, X. D. Zhang, J. Zhang, X. Yu, X. D. Guo, and B. H. Zhong, "Exposing {010} active facets by multiple-layer oriented stacking nanosheets for high-performance capacitive sodium-ion oxide cathode." *Adv. Mater.*, **30**, 1803765 (2018).
- J. W. Choi and D. Aurbach, "Promise and reality of post-lithium-ion batteries with high energy densities." *Nature Reviews Materials*, **1**, 1 (2016).
- H. Yang, H. Li, J. Li, Z. Sun, K. He, H. M. Cheng, and F. Li, "The rechargeable aluminum battery: opportunities and challenges." *Angew. Chem. Int. Ed.*, **58**, 11978 (2019).
- M. Angell, C.-J. Pan, Y. Rong, C. Yuan, M.-C. Lin, B.-J. Hwang, and H. Dai, "High Coulombic efficiency aluminum-ion battery using an AlCl_3 -urea ionic liquid analog electrolyte." *Proc. Natl. Acad. Sci.*, **114**, 834 (2017).
- T. Mori, Y. Orikasa, K. Nakanishi, C. Kezheng, M. Hattori, T. Ohta, and Y. Uchimoto, "Discharge/charge reaction mechanisms of FeS_2 cathode material for aluminum rechargeable batteries at 55° C." *J. Power Sources*, **313**, 9 (2016).
- H. Xu, T. Bai, H. Chen, F. Guo, J. Xi, T. Huang, S. Cai, X. Chu, J. Ling, and W. Gao, "Low-cost $\text{AlCl}_3/\text{Et}_3\text{NHCl}$ electrolyte for high-performance aluminum-ion battery." *Energy Storage Mater.*, **17**, 38 (2019).
- E. Pomerantseva, F. Bonaccorso, X. Feng, Y. Cui, and Y. Gogotsi, "Energy storage: the future enabled by nanomaterials." *Science*, **366**, eaan8285 (2019).
- J. Hassoun et al., "An advanced lithium-ion battery based on a graphene anode and a lithium iron phosphate cathode." *Nano Lett.*, **14**, 4901 (2014).
- D. Muñoz-Torrero, P. Leung, E. García-Quismondo, E. Ventosa, M. Anderson, J. Palma, and R. Marcilla, "Investigation of different anode materials for aluminium rechargeable batteries." *J. Power Sources*, **374**, 77 (2018).
- M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, and B.-J. Hwang, "An ultrafast rechargeable aluminium-ion battery." *Nature*, **520**, 324 (2015).
- N. Yabuuchi, K. Kubota, M. Dahbi, and S. Komaba, "Research development on sodium-ion batteries." *Chem. Rev.*, **114**, 11636 (2014).
- W. Wang, B. Jiang, W. Xiong, H. Sun, Z. Lin, L. Hu, J. Tu, J. Hou, H. Zhu, and S. Jiao, "A new cathode material for super-valent battery based on aluminium ion intercalation and deintercalation." *Sci. Rep.*, **3**, 3383 (2013).
- M.-C. Lin et al., "An ultrafast rechargeable aluminium-ion battery." *Nature*, **520**, 324 (2015).
- D.-Y. Wang et al., "Advanced rechargeable aluminium ion battery with a high-quality natural graphite cathode." *Nat. Commun.*, **8**, 14283 (2017).
- G. A. Elia, K. Marquardt, K. Hoepfner, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini, and R. Hahn, "An overview and future perspectives of aluminum batteries." *Adv. Mater.*, **28**, 7564 (2016).
- H. Yang, H. Li, J. Li, Z. Sun, K. He, H.-M. Cheng, and F. Li, "The rechargeable aluminum battery: opportunities and challenges." *Angew. Chem. Int. Ed.*, **58**, 11978 (2019).
- F. Wu, H. Yang, Y. Bai, and C. Wu, "Paving the path toward reliable cathode materials for aluminum-ion batteries." *Adv. Mater.*, **31**, 1806510 (2019).
- S. Gu, H. Wang, C. Wu, Y. Bai, H. Li, and F. Wu, "Confirming reversible Al^{3+} storage mechanism through intercalation of Al^{3+} into V_2O_3 nanowires in a rechargeable aluminum battery." *Energy Storage Mater.*, **6**, 9 (2017).
- N. Jayaprakash, S. K. Das, and L. A. Archer, "The rechargeable aluminum-ion battery." *Chem. Commun.*, **47**, 12610 (2011).
- S. Petnikota, J. J. Toh, J. Y. Li, R. Chua, and M. Srinivasan, "Citric acid assisted solid state synthesis of V_2O_3 , $\text{V}_2\text{O}_3/\text{C}$ and V_2O_3 /graphene composites for Li-ion battery anode applications." *ChemElectroChem*, **6**, 493 (2019).
- L. Jiang, Y. Qu, Z. Ren, P. Yu, D. Zhao, W. Zhou, L. Wang, and H. Fu, "In situ carbon-coated yolk-shell V_2O_3 microspheres for lithium-ion batteries." *ACS Applied Materials & Interfaces*, **7**, 1595 (2015).
- X. Li, J. Fu, Z. Pan, J. Su, J. Xu, B. Gao, X. Peng, L. Wang, X. Zhang, and P. K. Chu, "Peapod-like V_2O_3 nanorods encapsulated into carbon as binder-free and flexible electrodes in lithium-ion batteries." *J. Power Sources*, **331**, 58 (2016).
- Y. Zhang, A. Pan, S. Liang, T. Chen, Y. Tang, and X. Tan, "Reduced graphene oxide modified V_2O_3 with enhanced performance for lithium-ion battery." *Mater. Lett.*, **137**, 174 (2014).
- L. Kong, M. Zhong, Y. Liu, W. Xu, and X.-H. Bu, "Ultra-small V_2O_3 embedded N-doped porous carbon nanorods with superior cycle stability for sodium-ion capacitors." *J. Power Sources*, **405**, 37 (2018).
- T. Jin, H. Li, Y. Li, L. Jiao, and J. Chen, "Intercalation pseudocapacitance in flexible and self-standing V_2O_3 porous nanofibers for high-rate and ultra-stable K ion storage." *Nano Energy*, **50**, 462 (2018).
- V. Synček and F. Hanic, "The crystal structure of ammonium metavanadate." *Czechoslovakij fyzickij zurnal*, **4**, 120 (1954).
- G. Bauer, V. Güther, H. Hess, A. Otto, O. Roidl, H. Roller, and S. Sattelberger, "Vanadium and vanadium compounds." *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley, New York) (2000).
- K. Thushara, N. N. Binitha, and Y. Zahira, "Citric acid assisted facile synthesis of single phased crystalline micro vanadium pentoxide powder." *Aust. J. Basic Appl. Sci.*, **8**, 328 (2014), <http://ajbasweb.com/old/ajbas/2014/Special%2012/328-332.pdf>.
- Z.-H. Zhou, H. Zhang, Y.-Q. Jiang, D.-H. Lin, H.-L. Wan, and K.-R. Tsai, "Complexation between vanadium (V) and citrate: spectroscopic and structural characterization of a dinuclear vanadium (V) complex." *Transition Met. Chem.*, **24**, 605 (1999).
- A. E. Danks, S. R. Hall, and Z. Schnepf, "The evolution of 'sol-gel' chemistry as a technique for materials synthesis." *Materials Horizons*, **3**, 91 (2016).
- R. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides." *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
- N. N. Greenwood and A. Earnshaw (ed.), *Chemistry of the Elements* (Butterworth-Heinemann, Oxford) 2nd ed., p. 976 (1997).
- A. F. Wells, *Structural Inorganic Chemistry* (Oxford university press, United Kingdom) (2012).
- M. Chiku, H. Takeda, S. Matsumura, E. Higuchi, and H. Inoue, "Amorphous vanadium oxide/carbon composite positive electrode for rechargeable aluminum battery." *ACS Applied Materials & Interfaces*, **7**, 24385 (2015).
- B. V. Crist and D. B. Crist, *Handbook of Monochromatic XPS Spectra* (Wiley, New York) (2000).
- B. V. R. Chowdari, G. V. Subba Rao, and G. Y. H. Lee, "XPS and ionic conductivity studies on $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-(\text{TiO}_2 \text{ or } \text{GeO}_2)-\text{P}_2\text{O}_5$ glass-ceramics." *Solid State Ionics*, **136-137**, 1067 (2000).
- R. Baddour-Hadjean, E. Raelkelboom, and J. P. Pereira-Ramos, "New structural characterization of the $\text{Li}_x\text{V}_2\text{O}_5$ system provided by raman spectroscopy." *Chem. Mater.*, **18**, 3548 (2006).
- S. R. Desai, H. Wu, C. M. Rohlifing, and L.-S. Wang, "A study of the structure and bonding of small aluminum oxide clusters by photoelectron spectroscopy: Al_xO_y ($x=1-2$, $y=1-5$)." *J. Chem. Phys.*, **106**, 1309 (1997).

48. F. Ureña-Begara, A. Crunteanu, and J.-P. Raskin, "Raman and XPS characterization of vanadium oxide thin films with temperature." *Appl. Surf. Sci.*, **403**, 717 (2017).
49. L. D. Reed and E. Menke, "The roles of V_2O_5 and stainless steel in rechargeable Al-ion batteries." *J. Electrochem. Soc.*, **160**, A915 (2013).
50. T. Schoetz, M. Ueda, A. Bund, and C. Ponce de Leon, "Preparation and characterization of a rechargeable battery based on poly-(3,4-ethylenedioxythiophene) and aluminum in ionic liquids." *J. Solid State Electrochem.*, **21**, 3237 (2017).
51. S. Wang, Z. Yu, J. Tu, J. Wang, D. Tian, Y. Liu, and S. Jiao, "A novel aluminum-ion battery: $Al/AlCl_3$ -[EMIm]Cl/ Ni_3S_2 @Graphene." *Adv. Energy Mater.*, **6**, 1600137 (2016).
52. N. Canever, N. Bertrand, and T. Nann, "Acetamide: a low-cost alternative to alkyl imidazolium chlorides for aluminium-ion batteries." *Chem. Commun.*, **54**, 11725 (2018).
53. S. Wang, K. V. Kravchyk, F. Krumeich, and M. V. Kovalenko, "Kish graphite flakes as a cathode material for an aluminum chloride-graphite battery." *ACS Applied Materials & Interfaces*, **9**, 28478 (2017).
54. S. Petnikota, R. Chua, Y. Zhou, E. Edison, and M. Srinivasan, "Amorphous vanadium oxide thin films as stable performing cathodes of lithium and sodium-ion batteries." *Nanoscale Res. Lett.*, **13**, 363 (2018).
55. Z. A. Zafar, S. Imtiaz, R. Li, J. Zhang, R. Razaq, Y. Xin, Q. Li, Z. Zhang, and Y. Huang, "A super-long life rechargeable aluminum battery." *Solid State Ionics*, **320**, 70 (2018).
56. H. Wang, Y. Bai, S. Chen, X. Luo, C. Wu, F. Wu, J. Lu, and K. Amine, "Binder-free V_2O_5 cathode for greener rechargeable aluminum battery." *ACS Applied Materials & Interfaces*, **7**, 80 (2015).
57. P. Wang, H. Chen, N. Li, X. Zhang, S. Jiao, W.-L. Song, and D. Fang, "Dense graphene papers: toward stable and recoverable Al-ion battery cathodes with high volumetric and areal energy and power density." *Energy Storage Mater.*, **13**, 103 (2018).
58. G. A. Elia, I. Hasa, G. Greco, T. Diemant, K. Marquardt, K. Hoeppe, R. J. Behm, A. Hoell, S. Passerini, and R. Hahn, "Insights into the reversibility of aluminum graphite batteries." *Journal of Materials Chemistry A*, **5**, 9682 (2017).
59. S. Palumbo, L. Silvestri, A. Ansaldi, R. Brescia, F. Bonaccorso, and V. Pellegrini, "Silicon few-layer graphene nanocomposite as high-capacity and high-rate anode in lithium-ion batteries." *ACS Appl. Energy Mater.*, **2**, 1793 (2019).
60. E. Greco, G. Nava, R. Fathi, F. Fumagalli, A. E. Del Rio-Castillo, A. Ansaldi, S. Monaco, F. Bonaccorso, V. Pellegrini, and F. Di Fonzo, "Few-layer graphene improves silicon performance in Li-ion battery anodes." *Journal of Materials Chemistry A*, **5**, 19306 (2017).
61. Y. Liu, S. Sang, Q. Wu, Z. Lu, K. Liu, and H. Liu, "The electrochemical behavior of Cl^- assisted Al^{3+} insertion into titanium dioxide nanotube arrays in aqueous solution for aluminum ion batteries." *Electrochim. Acta*, **143**, 340 (2014).
62. P. Giridhar, S. Zein El Abedin, and F. Endres, "Electrodeposition of aluminium from 1-butyl-1-methylpyrrolidinium chloride/ $AlCl_3$ and mixtures with 1-ethyl-3-methylimidazolium chloride/ $AlCl_3$." *Electrochim. Acta*, **70**, 210 (2012).