Chemical lithiation studies on combustion synthesized V₂O₅ cathodes with full cell application for lithium ion batteries

Cheah, Yan Ling; Aravindan, Vanchiappan; Madhavi, Srinivasan

2013

Cheah, Y. L., Aravindan, V., & Madhavi, S. (2013). Chemical Lithiation Studies on Combustion Synthesized V₂O₅ Cathodes with Full Cell Application for Lithium Ion Batteries. *Journal of the Electrochemical Society*, 160(8), A1016-A1024.

<https://hdl.handle.net/10356/79542>

<https://doi.org/10.1149/2.015308jes>

© 2013 The Electrochemical Society. This paper was published in *Journal of the Electrochemical Society* and is made available as an electronic reprint (preprint) with permission of The Electrochemical Society. The paper can be found at the following official DOI: [<http://dx.doi.org/10.1149/2.015308jes>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 21:11:58 SGT

Chemical Lithiation Studies on Combustion Synthesized V_2O_5 Cathodes with Full Cell Application for Lithium Ion Batteries

Yan L. Cheah,^{a,b} Vanchiappan Aravindan,^b and Srinivasan Madhavi^{a,b,c,z}

^aSchool of Materials Science and Engineering, Nanyang Technological University, Singapore 639798

^bEnergy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore 637553

^cTUM-CREATE Center for Electromobility, Nanyang Technological University, Singapore 637553

Fundamental studies on Li-intercalation into layered vanadium pentoxide (V_2O_5), synthesized by urea combustion method, have been successfully carried out by chemical lithiation using butyl lithium at various concentrations. Morphological and structural changes during chemical lithiation are analyzed by field-emission scanning electron microscopy and X-ray diffraction measurements, respectively. Furthermore, chemical states and elemental concentration of these lithiated V_2O_5 phases were elucidated by X-ray photoelectron spectroscopy and inductively coupled plasma. Electrochemical studies *via* potentiostatic and galvanostatic modes show that the chemically-lithiated V_2O_5 phases undergo similar redox behavior as bare V_2O_5 at respective discharge-states. The electrochemical studies confirmed the occurrence of various phase transformations at various levels of discharge relating to both reduction of vanadium (V^{5+}) and intercalation of lithium ions in V_2O_5 . Finally, the full-cell comprising of lithiated V_2O_5 cathode and spinel $Li_4Ti_5O_{12}$ anode is demonstrated to study their compatibility toward insertion type anodes, delivering the reversible capacity of 80 mAh g^{-1} .

© 2013 The Electrochemical Society. [DOI: 10.1149/2.015308jes] All rights reserved.

Manuscript submitted March 12, 2013; revised manuscript received April 15, 2013. Published April 26, 2013.

Vanadium pentoxide (V_2O_5) is considered as one of the high capacity cathode materials for lithium-ion battery (LIB) applications.¹⁻⁴ Such high capacity cathodes comprising of multiple-electron reactions are anticipated for the development of high power Lithium-ion power packs for zero-emission vehicles, especially hybrid electric vehicles (HEV) and electric vehicles (EV).^{2,5} Multiple oxidation states of vanadium in V_2O_5 enable the intercalation of more than one Li per formula unit, thus giving rise to a capacity of >300 mAh g^{-1} .⁶⁻¹¹ The layered structure consisting of VO_5 octahedral units undergoes distortion during the accommodation of Li-ions, along with subsequent multiple reductions of transition metal vanadium from V^{5+} to a mixture of V^{4+} and V^{3+} .^{12,13} Generally, Li-intercalation into layered V_2O_5 is described according to the following equation,

In the first discharge, one can observe the multistep reduction process of vanadium occurring as prominent plateaus in galvanostatic discharge-charge and strong reduction peaks in the cyclic voltammetry studies. Formation of the different lithiated phases and reversibility of such phases can depend on the operating potential. Usually a first reduction peak (or plateau) occurs ~ 3.2 V vs. Li (OCV ~ 3.4 V vs. Li), indicating the reduction of V^{5+} to V^{4+} , which results in the formation of ϵ - $Li_xV_2O_5$ as described below,

Further reduction takes place at ~ 2.2 and 2.1 V vs. Li, corresponding to the partial reduction of V^{4+} to V^{3+} and results in the formation of mixed δ - and γ - $Li_xV_2O_5$ phases as given below

The observed phases, ϵ - $Li_{0.5}V_2O_5$ and δ - $Li_{1.0}V_2O_5$, are completely reversible during electrochemical charge-discharge process when the test cell is electrochemically cycled between 2-4 V vs. Li. Cycling below 2.0 V vs. Li results in irreversible γ - $Li_{2.0}V_2O_5$ formation at ~ 1.95 V (vs. Li). This irreversible reduction process of vanadium enables accommodation of more than two Li per formula unit. The continuous insertion of Li causes the distortion of V_2O_5 layers in order to accommodate more Li into the interlayer spaces between VO_5 octahedral units. At the end of first discharge, a distorted ω - Li - V_2O_5 structure forms without any prominent plateaus and hence only one pair of redox peaks are noted from CV studies.¹⁴⁻¹⁶

To further elucidate this, we made an attempt to lithiate the V_2O_5 phase chemically using butyl lithium and subsequently study the associated structural changes/phase transformations occurred *via* ex-situ studies. Mainly, chemical lithiation studies have been carried out only on bulk V_2O_5 powders.^{14,16-25} On the other hand, few reports are available for such chemically lithiated phases, for example Whittingham,²⁶ Garcia et al.²⁷ and Pecquenard et al.¹⁴ carried out lithiation in V_2O_5 using Butyl lithium solution and Murphy et al.²³ Rozier et al.²⁴ and Cocciantelli et al.^{18,28} conducted the lithiation using lithium iodide in acetonitrile at elevated temperatures. Moreover, Garcia et al.²⁷ prepared chemically-lithiated V_2O_5 phase in various concentrations and showed that the intercalation of lithium into V_2O_5 phase was reversible to certain extent whereas Pecquenard et al.¹⁴ mentioned that the phase transformation of $\delta \rightarrow \gamma$ - $Li_xV_2O_5$ was irreversible when x increases from <1 to >1 . On the other hand, Eguchi et al.²⁹ prepared Li - V_2O_5 phases using H_2O_2 and lithium and vanadium alkoxides in which $Li_{2.2}V_2O_5$ phase provides facile Li-insertion/extraction properties in terms of cycleability. Furthermore, Leger et al.³⁰ and Delmas et al.²⁰ discussed the applicability of ω - $Li_xV_2O_5$ as rechargeable cathode material in lithium ion batteries. Mai et al.³¹ also demonstrated the enhanced cycleability of lithiated phases of V_2O_5 . Studies on chemical lithiation into V_2O_5 phases clearly illustrate that pre-lithiation not only provide the information to understand the structural transformation, but also enable the enhanced cycleability during cycling. In the present work, a systematic study comprising the chemical Li-intercalation into urea-combustion synthesized V_2O_5 ⁶ along with direct correlations such as X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are carried out, and is also well-supported with electrochemical characterizations at various cutoff potentials. To the best of our knowledge, there exists several different observations^{16,21,24,32,33} with regards to the intercalation of lithium into V_2O_5 and it is possible that the Li intercalation to urea-combustion synthesized V_2O_5 could vary from the observations for bulk V_2O_5 . Moreover, the chemically-lithiated V_2O_5 phases were compared and confirmed with electrochemical lithiation in this work. Full-cell assembly was also conducted with spinel $Li_4Ti_5O_{12}$ anode and demonstrated for the reversible insertion of one mole lithium per V_2O_5 and described in detail.

Experimental

Sub-micron size V_2O_5 powders were obtained by urea-assisted combustion synthesis and described in our previous work.⁶ For chemical lithiation, V_2O_5 powder was dispersed in an appropriate amount of *n*-hexane (99%, Tedia) with stoichiometric proportions of *n*-butyl

^zE-mail: Madhavi@ntu.edu.sg

lithium (BuLi, 1.6 M in hexanes, Aldrich). Various concentrations, namely 0.2, 0.5, 1, 2 and 3 moles of BuLi per formula unit were used to obtain similar extent of lithiation as those of electrochemically lithiated samples ($\text{Li}_x\text{V}_2\text{O}_5$, $x = 0.2, 0.5, 1, 2$ and 3). For the concentrations below and above 1 moles of BuLi, the mixture was continuously stirred for 3 days and 1 week respectively, before being filtered and washed thoroughly with *n*-hexane. Then, the powders were dried and stored in an Argon-filled glove box (MBraun Unilab, Germany) until further characterization and electrochemical studies. Due to the severe reactive nature of BuLi toward air, the entire process of chemical lithiation was carried out in the glove box. For clarity, the obtained samples are denoted as Li0.2, Li0.5, Li1, Li2 and Li3 in relation to the stoichiometric amount of chemically-inserted Li per V_2O_5 .

Morphological features of lithiated V_2O_5 powders were analyzed by field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F). Powder X-ray diffraction measurements was carried out to study the structural properties of the lithiated V_2O_5 using D8 Advance instrument (Bruker) equipped with $\text{Cu-K}\alpha$ radiation. Rietveld refinement was also conducted for the obtained reflections using Topas V3 software. X-ray photoelectron spectroscopy (XPS) was performed with an Axis Ultra (Kratos) spectrometer with monochromatic Al- $\text{K}\alpha$ excitation and analyzed using CasaXPS software (Version 2.3.15). Inductively-coupled plasma (ICP) analysis (Agilent 7700, Japan) was also carried out on acid-digested solutions of lithiated V_2O_5 powders.

Composite cathodes were fabricated by mixing active material (bare/lithiated V_2O_5), binder (Kynar 2801), and conductive additive (Super P Li carbon, Timcal) in the weight ratio 60:20:20, respectively (active material loading of $\sim 5\text{--}7$ mg). 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich) was used as solvent to dissolve binder to form slurry and the mixture was continuously stirred. The resulting viscous slurry was subsequently coated over aluminum foil (Al) using a doctor blade. The coated Al foils were dried in a vacuum oven for several hours to remove the trace amount of solvents, if any. Then the composite electrodes were pressed between twin rollers to provide necessary adherence toward Al current collector. The dried composite electrodes were punched out with 16 mm diameter blanks and same area of counter electrode lithium foil (~ 0.59 mm thick, Hohsen Corporation, Japan) was used to construct the test cells. Li-insertion properties were evaluated in half-cell configuration using two-electrode CR 2016 coin cell assembly. The coin-cells were fabricated in an Argon-filled glove box and the electrodes were separated by Celgard 2400 separator. 1 M LiPF_6 in ethylene carbonate (EC): dimethyl carbonate (DMC) (Selectipure LP30, Merck KGaA, Germany) mixture was used as electrolyte solution.

For the full-cell assembly, test electrodes were formulated with active material (V_2O_5 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$), teflonized acetylene black (TAB-2, Hohsen Corporation, Japan), and conductive additive (Super P Li carbon, Timcal) using ethanol as the solvent. The test electrodes were pressed into a 200 mm^2 stainless steel mesh which served as current collector. The composite electrodes were subsequently dried at 60°C for overnight before conducting cell assembly in Argon glove box. Before conducting full-cell assembly, Li-insertion properties of V_2O_5 were evaluated in half-cell configurations by restricting the potential window to 2.5–4 V vs. Li for insertion/extraction of one mole of Li. Native V_2O_5 was first electrochemically lithiated using the Swagelok cells and discharged to 2.5 V vs. Li at current density of 10 mA g^{-1} . Based on the electrochemical performance of the bare V_2O_5 powder (electrochemical lithiation) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in half-cell configuration, the optimized mass ratio between cathodes to anode is fixed at 1:0.68 (5 mg: 3.4 mg). Then, the full-cell, comprising of electrochemically-lithiated V_2O_5 (LiV_2O_5) phase as cathode and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode under the optimized mass loadings, was assembled. Galvanostatic cycling profiles were recorded for both half- and full-cell configurations in ambient temperature conditions using battery testing systems (Neware). Cyclic voltammetry (CV) was recorded using Solartron 1470E potentiostat using standard two-electrode configuration at slow scan rate of 0.1 mV s^{-1} .

Figure 1. Field-emission scanning electron microscope (FE-SEM) images of (a) bare V_2O_5 , (b) Li0.2, (c) Li0.5, (d) Li1, (e) Li2 and (f) Li3.

Results and Discussion

Surface morphology of the bare and chemically-lithiated V_2O_5 powders were analyzed by FE-SEM and shown in Figure 1. From Figure 1, it is observed that bare V_2O_5 , Li0.2 and Li0.5 powders are exhibiting irregularly-shaped particulate morphology (Figure 1a–1c respectively), which indicates that smaller amounts of Li-intercalation did not affect the morphological features of the native compound. When the concentration exceeds 0.5 moles of Li, changes in the surface morphology is noted (Figure 1d–1f). This can be inferred that, urea-combustion synthesized V_2O_5 undergoes a structural change to accommodate >1 moles of Li per formula unit. Particulate morphology is observed to be completely collapsed for the case of Li2 (Figure 1e) and converted into needle-like morphology for Li3. It can be observed that the powder-like morphology is no longer present for higher amount of Li-insertion (2–3 Li per V_2O_5).

Powder XRD patterns were recorded to study the structural changes that had occurred during chemical lithiation in V_2O_5 and presented in Figure 2. From Figure 2a, the presence of new peaks at 2θ values ~ 20 and $\sim 21^\circ$ for 0.2 moles of Li-insertion (Li0.2) is clearly noticeable. To understand reason for the appearance of such peak, Rietveld refinement was conducted and presented in Figures 2b and 2c. Interestingly, the extra peak also belongs to the *Shcherbinaite* (space group $Pmn2_1$) phase of V_2O_5 with relatively larger crystallites. Figuratively, two V_2O_5 phases sharing the same crystal structure was observed to be formed at lower level of chemical lithiation (Li0.2). Variation in the lattice parameter values is also noted between the two phases of V_2O_5 ; the lattice parameter values of first native *Shcherbinaite* phase is $a = 11.435$ (1) Å, $b = 4.487$ (3) Å, $c = 3.569$ (4) Å with crystallite size of ~ 103 nm and the second similar phase containing $a = 11.503$ (6) Å, $b = 4.393$ (1) Å and $c = 3.567$ (1) Å as lattice parameter with crystallite size of ~ 155 nm. It is possible that lithiation occurred partially in the V_2O_5 phase which leads to increase

Figure 2. (a) X-ray diffraction (XRD) of bare and chemically-lithiated V_2O_5 samples and Rietveld refinement of (b) Li0.2 and (c) Li1.

in the lattice parameter a values, whereas slight reduction in the values is noted for b and c axis. The larger crystal size could be an indication of the emergence of phase change. It is evident that, in Li0.2, only partial Li-intercalation occurs which leads to the mixed formation of lithiated and non-lithiated V_2O_5 phases. When the lithium concentration in V_2O_5 is increased to 0.5 moles in Li0.5, the XRD pattern showed an extra reflection at $\sim 18^\circ$ 2θ along with peaks related to the V_2O_5 structure. Observed reflections were subjected to Rietveld refinement which indicates the existence of two phases, i.e. native V_2O_5 phase and a $Li_xV_2O_5$ phase, with $Pnma$ space group. The respective lattice parameters of the two phases are derived from refinement and found to be $a = 11.411$ (2) Å, $b = 4.515$ (4) Å and $c = 3.568$ (1) Å with crystallite size of ~ 72 nm for native V_2O_5 phase (Shcherbinaite structure with $Pmn2_1$ space group) and the second phase $Li_xV_2O_5$ showing the lattice parameter values of $a = 9.942$ (1) Å, $b = 3.638$ (3) Å and $c = 9.908$ (1) Å with crystallite size of ~ 100 nm ($Pnma$ space group). It is evident that the c values of both phases are entirely different because of the large distortion of the V_2O_5 structure upon Li-intercalation. The observed changes in the lattice parameters are in agreement with the observations by Cocciantelli et al.,³⁴ and in addition the noted phase transition from α - V_2O_5 to ϵ - $Li_{0.5}V_2O_5$ is in agreement with the discussion by Katze et al.,²² which proposes the partial intercalation of Li, related to the emerging perturbation of the layered structure of V_2O_5 . In Li1, further deviation from the lattice parameter values are noted particularly in c -axis ($Pnma$, $a = 9.623$ (3) Å, $b = 3.780$ (4) Å and $c = 10.341$ (9) Å with crystallite size of ~ 49 nm). This can be correlated to the formation of ϵ - LiV_2O_5 phase²¹ and well supported by Rietveld refinement (Figure 2b). During electrochemical studies, in the half-cell configuration of native V_2O_5 (Li/ V_2O_5), discharging to ~ 2.5 V vs. Li leads to the formation of the said phase which cor-

Figure 3. Representative X-ray photoelectron spectroscopy (XPS) (Li 1s) of chemically-lithiated V_2O_5 powders.

responds to one mole Li-insertion and the formation of such phase has been confirmed during electrochemical lithiation by us and other researchers as well.^{6,35,36} When the concentration exceeds beyond 1 mole of Li, the formation of an amorphous phase results, as observed in Li2, and can be correlated to the beginning of the irreversible phase change^{19,34} via lithium intercalation. Lithiation of 3 moles of BuLi per V_2O_5 formula unit (Li3) leads to the phase transformations into the heavily lithiated V_2O_5 phase. The observed peaks for Li3 could be matched to that of $Li_xV_2O_5$ phase which indicates the reformation of a distorted V_2O_5 structure with large accommodation of Li^+ ions.²³ This phase is assumed to the ω - $Li_{2.2}V_2O_5$ phase and such irreversible phase is usually formed at the end of first electrochemical lithiation of V_2O_5 phase in half-cell configuration at below 2.0 V vs. Li.^{20,21}

To support the presence of Li in the chemically-lithiated phases, XPS was carried out for all the V_2O_5 powders and a representative spectrum is shown in Figure 3. Peaks can be observed in all the lithiated phases at ~ 55.7 eV which is similar to that of lithium vanadate compound³⁷ Though the presence of Li in the V_2O_5 phases has been confirmed through XPS. However, it is too difficult to determine the exact amount of Li present in the phases, since XPS is a surface sensitive technique. Therefore, the amount of Li present in the V_2O_5 was further analyzed using inductively coupled plasma (ICP) and presented in Table I. For Li0.2 and Li0.5, the Li:V ratio are in good agreement with the concentrations of both BuLi and V_2O_5 used (Table I). However in the case of Li1 and Li2, the amount of Li present in the V_2O_5 phases is slightly higher than the calculated stoichiometric ratio of chemically-inserted Li. Taking into consideration that the highest report amount of Li that can be intercalated per V_2O_5 is 3, to give ω - $Li_3V_2O_5$,^{20,21,29} it is safe to say that the intercalation of 4 Li per V_2O_5 in Li2 is not possible. This clearly indicates that there is a phase change occurring in the layered V_2O_5 structure to accommodate more Li into the V_2O_5 structure, since it is too complicated to control the concentration of lithiation into layered phase by chemical route. The excess Li that is observed via ICP lends support to the hypothesis that the layered structure of V_2O_5 has broken down at this point. The

Table I. Summary of ICP analyses.

Lithiated phase	Li:V ratio
Li0.2	1.4:10
Li0.5	1:4
Li1	8:10
Li2	2:1
Li3	2.5:2

lower amount of vanadium could be possibly attributed to the washing away of unreacted vanadium salts during filtration, as well as the formation of amorphous, or poorly crystalline, lithium vanadate compounds such as those mentioned by Rozier et al.²⁴ which cannot be detected *via* XRD. Moreover, the observations from the ICP results are in good agreement with XRD reflections (Figure 2) up to Li2, where the structure is rendered nearly amorphous after reacting with 2 moles of BuLi. The maximum amount of lithiation is found to be ~ 2.5 moles of Li per V_2O_5 formula unit for Li3. The fully-lithiated formula of $Li_x V_2O_5$ can be thus derived to be the ω - $Li_{2.5}V_2O_5$.^{20,21}

Electrochemical properties of the chemically-lithiated V_2O_5 phases were studied along with bare V_2O_5 ; hence the half-cell assembly was performed for all the phases (Li0.2 through Li3). The half-cells comprising lithiated V_2O_5 phases were first charged to 4.0 V vs. Li to extract the chemically-inserted Li and then subsequently discharged for re-insertion and presented in Figure 4. For the comparison purposes, CV traces of bare V_2O_5 were also conducted and presented in Figures 4a and 4b. In the 1st cycle (Figure 4a), multiple oxidation/reduction peaks are observed which corresponds to the intercalation/de-intercalation processes of Li^+ in V_2O_5 . The reduction (cathodic) peaks are observed at ~ 3.37 , ~ 3.16 , ~ 2.22 , and ~ 1.81 V vs. Li, whereas only two oxidation peaks are observed at ~ 2.70 and ~ 3.45 V vs. Li during the anodic sweep. The cathodic peaks at ~ 3.37 and ~ 3.16 V vs. Li indicate the reduction of V^{5+} to V^{4+} which leads to the formation of ϵ - $Li_x V_2O_5$ phase. The other cathodic peaks at ~ 2.22 and ~ 1.81 V vs. Li belongs to the partial reduction of V^{4+} to V^{3+} , and this reduction reveals the formation of δ - and γ - $Li_x V_2O_5$ mixed phases. Cycling below 2.0 V vs. Li results in the formation of irreversible γ - $Li_x V_2O_5$ phase which is confirmed by the appearance of reduction peak at ~ 1.81 V vs. Li.^{6,35} This reduction process enables the accommodation of more than 2 moles of Li per V_2O_5 formula unit. However, reversible reactions take place only at the potentials of ~ 2.70 and ~ 3.45 V vs. Li during anodic scan. During subsequent cycles (Figure 4b), only one well-defined oxidation/reduction pair is present for V_2O_5 . Further, the reduction peak is shifted to ~ 2.42 V vs. Li, whereas oxidation peak remains at ~ 2.84 V vs. Li. These peaks are intact upon further cycling to 20 cycles, indicating good reversibility during the redox reactions, while the small reduction of net charge under the curve can be correlated to capacity fading during cycling. The CV traces of Li0.2 and Li0.5 showed similar peaks to that of bare V_2O_5 with variation in the peak currents. However it is obvious that the reduction peaks at ~ 3.35 and ~ 3.12 V vs. Li in the first cycle are more pronounced for both lithiated phases than bare V_2O_5 . In the case of Li0.5, an additional oxidation peak at 3.4 V vs. Li is noted with small peak current. The presence of such new peak is attributed to the existence of LiV_2O_5 phase which is well supported from the XRD measurements but in the subsequent cycles, the performance is similar to that of bare V_2O_5 . When the concentration is increased to 1 mole of BuLi (Li1), the completion of LiV_2O_5 phase takes place. In the first cycle (Figure 4g), one oxidation and two reduction peaks are noted at 2.70 V vs. Li and 3.25 & 2.42 V vs. Li respectively. The absence of other peaks infers the disappearance of native V_2O_5 phase and confirms the structural change upon intercalation of 1 mole of Li. In the second cycle onwards (Figure 4h), oxidation peaks are observed at 2.70, 3.16 and 3.50 V vs. Li whereas reduction peaks are evidenced at 3.30 V and 2.43 V vs. Li. The overall areas of the CV traces are reduced by one order compared to bare V_2O_5 . Upon further cycling to 10 cycles, suppression of oxidation peaks (3.50 and 2.70 V vs. Li) and shifting of reduction peaks from 3.30 to 3.17 V vs. Li are noted along with the reduction in the area underneath the curve. At the 5th cycle extra peaks at 2.15 and 1.94 V vs. Li are observed. The appearance and disappearance of the peaks during subsequent cycles are an indication that several irreversible reactions may occur in subsequent redox reactions.

According to the XRD, lithiation of beyond 2 moles of Li into V_2O_5 (Li2) leads to the formation of an amorphous phase. In the first cycle (Figure 4i), two main oxidation peaks are observed at 2.90 and 3.48 V vs. Li while main reduction peaks are observed at 3.38, 3.18, 2.30 and 1.90 V vs. Li. The presence of several small redox peaks in

the CV may indicate the occurrence of Li-insertion/extraction into the disordered structure of Li2. The area under the CV curves is relatively small, which is similar to one mole Bu Li lithiated phase. Presence of Li inside the layered V_2O_5 structure could lead to overall reduced initial capacity which results possible insertion of fewer amounts of Li by electrochemical routes. Subsequent cycling to 10 cycles (Figure 4j), showed the oxidation peak remained at 2.90 V vs. Li, and broadening of peak potential at 3.48 V vs. Li are evident and encompassing the other small peaks noted initially. Disappearance of reduction peaks at 3.38 and 3.18 V vs. Li are noted with reduced intensity at 10th cycle and shifting of peak at 2.30 to 2.14 V vs. Li also evidenced. However, reduction potential at 1.93 V vs. Li appears only in the first cycle and disappeared in successive cycles, indicative of an irreversible reaction. On the other hand, chemical-intercalation of high concentration (Li3) of lithium into V_2O_5 matrix leads to the formation of $Li_3V_2O_5$ phase (theoretically), in which the first cycle of the CV (Figure 4k) shows oxidation peaks at ~ 2.30 , 2.60, 3.33, 3.46, 3.50 and 3.66 V vs. Li with forming corresponding redox pairs and peaks potentials at ~ 2.33 , 2.40, 3.16, 3.37, 3.45 and 3.60 V vs. Li. The oxidation peaks appear at similar voltages to the reduction peaks of bare V_2O_5 , indicating the de-intercalation of the chemically-lithiated Li ions with less polarization. The absence of oxidation peak at 1.90 V vs. Li at the first cycle of CV for Li3 ($Li_{2.5}V_2O_5$) indicates the irreversible phase transformation of V_2O_5 structure when the insertion of Li exceeds 2 moles. Subsequent cycles (Figure 4l) only show two pairs of redox peaks at 2.69/2.45 (ox/red) and 2.33/1.90 V vs. Li respectively, indicating that subsequent electrochemical Li-intercalation/de-intercalation occur reversibly without any noticeable plateaus.

Cycling performances of chemically-lithiated V_2O_5 phases were also studied in galvanostatic mode between 1.75–4 V vs. Li in ambient temperature conditions and given in Figure 5. The chemically-lithiated V_2O_5 cathodes were first charged at constant current rate (0.05 C, ~ 15 mA g^{-1}) to 4.0 V vs. Li to extract the chemically inserted Li into the V_2O_5 structure. The first charge cycles are presented in Figure 5a. The first charge capacities of 26, 66 and 70 mAh g^{-1} is observed for Li0.2, Li0.5 and Li1, and corresponds to the de-intercalation of 0.18, 0.45 and 0.48 moles of lithium, respectively. More importantly, the observed values are reversible reinsertion of lithium ions, as opposed to chemically intercalated lithium, while the slight differences between the chemically intercalated Li and the electrochemically extracted Li could be attributed to the in homogeneity of Li insertion as observed in the XRD. Noticeable difference is observed for Li1 which may be due to the formation of LiV_2O_5 structure (as observed in the XRD), leading to strong bonding between Li ions and VO_5 octahedral units. Hence, the de-lithiation of Li from LiV_2O_5 may not be fully reversible during charge process in the first cycle. This result is similar to Garcia et al.²⁷ in which the incomplete Li-re-insertion was noted during chemical lithiation when the concentration is beyond 0.9 moles of Li per formula unit. On the other hand, at higher concentrations of BuLi, a similar kind of irreversibility is noted, for example 0.68 and 0.85 moles of Li is reversible for Li2 and Li3, respectively. Apart from the irreversibility of chemically-inserted Li, the amorphization of the crystal structure cannot be ruled out for such poor irreversibility at higher concentrations. Subsequent galvanostatic charge-discharge cycles of the chemically-lithiated V_2O_5 phases are presented in Figures 5b and 5c. For Li0.2 and Li0.5, it can be observed that the discharge curves and capacities are similar to that of bare V_2O_5 , since the chemically-intercalated Li is highly reversible in lower concentrations. In the first discharge, the maximum lithiation are found to be ~ 2.4 , ~ 2.5 and ~ 2.2 Li for Li0.2, Li0.5 and bare V_2O_5 , respectively. This clearly indicates similar Li-intercalation processes occurred during the first discharge for said phases and eventually leads to the formation of irreversible ω - $Li_{2.5}V_2O_5$ phase when the testing potential decreases to < 2.0 V vs. Li. In contrast, lower concentrations of Li-insertion (Li0.2 and Li0.5) did not affect the structural properties of V_2O_5 drastically; however, insertion of > 2 moles of Li per formula unit certainly influences the structural properties of V_2O_5 . At higher concentrations of Li insertion (1, 2 and 3 moles), no obvious plateaus can be observed in the galvanostatic traces. It is interesting to note

Figure 4. Representative cyclic voltammograms (CV) showing first and subsequent cycles of urea combustion synthesized V_2O_5 powders with different amount of lithiation (a) & (b) bare V_2O_5 , (c) & (d) $Li_{0.2}$, (e) & (f) $Li_{0.5}$, (g) & (h) Li_1 , (i) & (j) Li_2 , (k) & (l) Li_3 respectively.

Figure 5. Typical charge-discharge profiles of combustion synthesized V_2O_5 cathodes (a) First charge curves of V_2O_5 cathodes with different amount of chemical lithiation at 15 mA g^{-1} , (b) First discharge profiles of V_2O_5 cathodes with different amount of chemical lithiation (c) second charge-discharge curves at 30 mA g^{-1} of chemically lithiated V_2O_5 cathodes.

that much lower initial discharge capacities of ~ 210 (1.4 moles of Li) and ~ 88 (0.6 moles of Li) mAh g^{-1} noted in Li1 and Li2. Possible amorphization could occur during chemical insertion of higher concentration of Li which cause structural change and results in overall lower intercalation of Li in the lithiated phases. In Li3, formation of $\omega\text{-Li}_x\text{V}_2\text{O}_5$ phase is inevitable and hence there is no obvious plateaus are noted, which is similar to the second discharge curves of bare V_2O_5 . It is noteworthy that the highly-distorted structure of $\text{Li}_{2.5}\text{V}_2\text{O}_5$ (Li3) formed *via* chemical lithiation, which enables the accommodation of ~ 2.2 moles of Li per formula unit, has a slightly increased discharge capacity value of $\sim 330 \text{ mAh g}^{-1}$ as compared to bare V_2O_5 ($\sim 320 \text{ mAh g}^{-1}$). As observed in Figure 5c, there are no obvious plateaus in all the second charge-discharge curves irrespective of the BuLi concentration and similar kind of traces are noted in subsequent charge cycles. The second charge capacities of ~ 334 (~ 2.25 moles of Li), ~ 348 (~ 2.3 moles of Li), ~ 190 (~ 1.3 moles of Li), ~ 80 (~ 0.6 moles of Li) and $\sim 325 \text{ mAh g}^{-1}$ (~ 2.2 moles of Li) for Li0.2, Li0.5, Li1, Li2 and Li3 were observed respectively, compared to the first charge capacity of bare V_2O_5 ($\sim 290 \text{ mAh g}^{-1}$ equivalent to ~ 2 moles of Li).

The galvanostatic cycling studies were continued up to 50 cycles at 0.1 C (30 mAh g^{-1}) rate in room temperature and given in Figure 6a. It can be seen from Figure 6a, Li0.2, Li0.5, and Li3 phases delivered higher initial capacities than bare V_2O_5 in the initial cycles and remains so after 50 cycles. The higher initial capacity in lithiated phases could be attributed to the presence of chemically-intercalated Li-ions present in the V_2O_5 lattice. It is also interesting to note that the large capacity drop ($\leq 20\%$ of initial capacity) is noted between first and second discharge capacities especially for bare V_2O_5 , Li0.2 and Li1. The large irreversible discharge capacity difference in V_2O_5 cathodes is expected and it is correlated to the irreversible phase transformation occurring at the end of the first discharge when the lower cutoff poten-

Figure 6. Plot of discharge capacity vs. cycle number for chemically-lithiated V_2O_5 cathodes cycled between different potential windows (a) $1.75\text{--}4.0 \text{ V vs. Li}$ and (b) $3.0\text{--}4.0 \text{ V vs. Li}$, both at current density of 30 mA g^{-1} .

tial is beyond 2 V vs. Li . For Li0.2 this phenomena can be correlated to the similarity of the structure to that of bare V_2O_5 , and for Li1 it can be noted that approximately ~ 0.5 mol of Li (from chemical lithiation) is retained in the structure after electrochemical de-lithiation in the first galvanostatic charge. No irreversible phase changes are noted from the second discharge onwards for lithiated V_2O_5 (electrochemically during discharge); therefore the capacity fades more gently upon subsequent cycles. Also, the low initial capacity of Li2 can be attributed to its amorphous structure, which is not ideal for Li-intercalation/de-intercalation. In the case of Li3, only 2% difference between the first and second discharge capacity values is noted. A lower level of chemical lithiation (Li0.2 and Li0.5) certainly improves the cycleability which is consistent with the literature.^{27,31} Irrespective of the phases, capacity fading is inevitable during cycling between $1.75\text{--}4 \text{ V vs. Li}$ with structural destruction as well. Hence, an attempt has been made to improve the cycleability of $\text{Li}_x\text{V}_2\text{O}_5$ cathodes by restricting them for one mole of Li-insertion/extraction by adjusting the lower cutoff potential ($3\text{--}4 \text{ V}$ and $2.5\text{--}4 \text{ V vs. Li}$) without destroying the crystal structure.

Galvanostatic cycling profiles were carried out in half-cell configurations for all the phases between $3\text{--}4 \text{ V vs. Li}$ at constant current density of 30 mA g^{-1} and given in Figure 6b. The narrow potential window enables facile reversible Li-insertion/extraction without the formation of irreversible phase by compromising the discharge capacity. All the chemically lithiated phases reversibly extracted, at most, less than one mole of Li per formula unit irrespective of the BuLi concentration. Therefore, it is logical to assume that the cycleability can be expected to be quite stable between such narrow potential windows. From the cycling profile, the performance of Li0.2 is different in the narrow potential window, as compared to the testing potential range of $1.75\text{--}4.0 \text{ V vs. Li}$. The Li0.2 phase delivered the reversible capacity of $\sim 70 \text{ mAh g}^{-1}$ with corresponding theoretical capacity of 147 mAh g^{-1} for one mole Li reaction. In all the cases, very stable cycling profiles are observed for tested 50 cycles, among them Li0.5 is found to be a high performing electrode material. Though the lithiated phases delivered appreciable performance in the half-cell configuration in narrow potential window, it is too difficult to quantitatively control the Li concentration during chemical lithiation. Hence, electrochemical lithiation has been carried out for reversible insertion of one mole Li and compared with the selected composition of chemically-lithiated V_2O_5 phase (LiV_2O_5).

The half-cell assembly ($\text{Li}/\text{V}_2\text{O}_5$) was fabricated to evaluate the electrochemical performance in both galvanostatic and

Figure 7. Cyclic voltammograms (CV) of (a) bare V_2O_5 cycled for the reversible insertion of one mole Li electrochemically and (b) LiV_2O_5 powders, tested between 2.5–4.0 V vs. Li in half-cell configuration at scan rate of 0.1 mV s^{-1} .

potentiostatic modes between 2.5–4 V vs. Li in ambient conditions. Electrochemical performance of chemically lithiated phase (Li_1 , equivalent to $\delta\text{-Li}_{1.0}\text{V}_2\text{O}_5$) is also investigated for comparison. Family of CV traces has been recorded at slow scan rate of 0.1 mV s^{-1} for both materials, in which metallic lithium acts as both counter and reference electrode and illustrated in Figure 7. The CV curves of bare V_2O_5 half-cell (Figure 7a) shows reduction peaks at ~ 3.36 , ~ 3.15 and ~ 2.60 V vs. Li respectively during electrochemical lithiation which is indicative of reduction of V^{5+} (present in V_2O_5) to a mixture of V^{4+} and V^{3+} and subsequent intercalation of Li. A mixture of δ and $\epsilon\text{-Li}_x\text{V}_2\text{O}_5$ is formed while discharging to 2.5 V vs. Li. Upon charging, oxidation peaks are observed at ~ 3.26 , 3.37 and 3.47 V vs. Li respectively, indicative of the reversibility of the Li intercalation/de-intercalation processes during anodic sweep. Subsequent cycling of the bare V_2O_5 half-cell shows minimal fading with no change in the peak potential. This clearly shows that the reactions are highly reversible throughout the cycling process and it is possible that electrochemical cycling within the 2.5–4 V vs. Li range maintains excellent cyclic retention properties in the V_2O_5 electrode material. On the other hand, CV curves of LiV_2O_5 were recorded under the same testing conditions and presented in Figure 7b. Only one pair of less intense redox peaks are observed at ~ 3.55 (ox) and ~ 3.14 (red) V vs. Li respectively. This indicates reversible formation of the LiV_2O_5 structure which enables facile Li-insertion/extraction. As observed in both CV traces, the mirrored-redox peaks indicate the excellent reversibility of both V_2O_5 phase during electrochemical cycling.

Galvanostatic cycling was also conducted within the voltage range of 2.5–4 V vs. Li at current density of 10 mA g^{-1} and presented in Figure 8. The typical charge-discharge profiles of bare V_2O_5 (Figure 8a) show two prominent plateaus both in discharge and charge

Figure 8. Typical galvanostatic charge-discharge traces of (a) bare V_2O_5 and (b) LiV_2O_5 powders in half-cell configuration 2.5–4.0 V vs. Li at constant current density of 10 mA g^{-1} . (c) Plot of discharge capacity vs. cycle number for LiV_2O_5 and at different scan rate for bare V_2O_5 .

process. The discharge plateaus are observed at ~ 3.39 and 3.18 V vs. Li, while charge plateaus are noted at ~ 3.29 and 3.42 V vs. Li. The observed prominent plateaus are in good agreement with the CV traces and the discharge capacity of $\sim 115 \text{ mAh g}^{-1}$ was observed. On the other hand, LiV_2O_5 half-cell (vs. Li) delivered the discharge capacity of $\sim 140 \text{ mAh g}^{-1}$ at current density of 10 mA g^{-1} . However, very small monotonous plateaus could be observed at ~ 3.2 – 3.6 V in discharge (Figure 8b) and a similar kind of plateau is present at ~ 3.1 – 3.6 V during charge process. This clearly indicates reversible Li-insertion/extraction in both chemically and electrochemically lithiated phases of V_2O_5 and is supported well with the CV measurements. The plot of discharge capacity vs. cycle number is presented in Figure 8c. It can be observed that the chemically-lithiated phase (LiV_2O_5) undergoes larger capacity fading during cycling, as compared to native V_2O_5 which exhibits stable capacity throughout 50 cycles even at high currents of 30 mA g^{-1} between 2.5–4 V vs. Li. The initial increasing trend of cycling behavior of native phase (at gravimetric current rate of 10 mA g^{-1}) is mainly attributed to the slower participation of active material during electrochemical reaction.

To demonstrate the performance of urea-combustion synthesized V_2O_5 powder in practical cells, a full-cell assembly is conducted with commercially available spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. For the full-cell assembly, mass balance between the electrodes is very crucial to attain high performance cells. In comparing the electrochemical performance of the chemically and electrochemically lithiated phases, the latter is found to be a better performing electrode material in the half-cell configuration in terms of cyclic stability. Similarly, half-cell assembly was conducted for commercially available $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$) under the same current density between 3–1 V vs. Li for the mass optimization. Based on the electrochemical performances

Figure 9. Cyclic voltammograms (CV) of full cell consisting of V_2O_5 cathode and lithium titanate spinel ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anode at 0.1 mV s^{-1} .

of the bare V_2O_5 powder (electrochemical lithiation) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in half-cell configuration, the mass ratio between cathodes to anode is fixed at 1:0.68 for optimum performance. Bare V_2O_5 was electrochemically lithiated using the Swagelok fittings and discharged to 2.5 V vs. Li at current density of 10 mA g^{-1} . Full-cell, $\text{LiV}_2\text{O}_5/\text{Li}_4\text{Ti}_5\text{O}_{12}$ is constructed with electrochemically lithiated V_2O_5 (LiV_2O_5) phase and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and cycled between 1–2.5 V in ambient temperature conditions.

CV traces were recorded at slow scan rate of 0.1 mV s^{-1} to elucidate the redox reactions and presented in Figure 9. The full-cell is charged first to extract the Li-ions from LiV_2O_5 and two oxidation peaks at ~ 1.68 and 1.91 V confirmed the oxidation of transition metal V^{4+} in to V^{5+} in a two-step manner. Upon discharging, two reduction peaks at ~ 1.80 and 1.58 V correspond to the reduction of V^{4+} to V^{5+} from V_2O_5 . The oxidation process is attributed to the removal of Li from LiV_2O_5 and subsequent insertion in to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice, whereas the said process is reversed during the reduction reaction. Galvanostatic cycling studies were conducted for full-cell assembly and tested between 1–2.5 V at constant current density of 20 mA g^{-1} and shown in Figure 10. The full-cell showed plateaus at ~ 1.84 and

Figure 10. (a) Typical galvanostatic traces of, and (b) discharge capacity vs. cycle number of full cell, comprising of electrochemically lithiated V_2O_5 and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anode.

$\sim 1.61 \text{ V}$ in discharge and corresponding charge plateaus are noted at ~ 1.75 and $\sim 1.88 \text{ V}$. These plateaus are indicative of the reduction and oxidation reactions occurring in the electrochemically-lithiated V_2O_5 powder which is in good agreement with those of the V_2O_5 half-cell data (Figure 7a). The full cell of $\text{LiV}_2\text{O}_5/\text{Li}_4\text{Ti}_5\text{O}_{12}$ delivered the capacity of ~ 92 (~ 0.63 moles of Li) and 75 (~ 0.51 moles of Li) mAh g^{-1} for first charge and discharge, respectively. Except for the first few cycles, the coulombic efficiency is found to be $>98\%$. However, capacity fading is the main issue for electrochemically lithiated V_2O_5 and retained the 67% of initial discharge capacity with operating potential of $\sim 1.75 \text{ V}$. The observed capacity trends are slightly poor compared to the electrochemically lithiated one dimensional electrospun V_2O_5 nanofibers cathodes when coupled with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode.³⁸

In general, this chemical-lithiation study on urea combustion synthesized V_2O_5 powder provides a deeper understanding of the Li intercalation mechanism into V_2O_5 lattice by chemical lithiation, with comparison to electrochemically-lithiated phase. Interestingly, in contrast to the work by Rozier et al.,²⁴ the current experiments show the formation of mixtures comprising of only $\text{Li}_x\text{V}_2\text{O}_5$ ($Pnma$) and V_2O_5 ($Pmn2_1$) phases, instead of other lithium vanadate and vanadate compounds. Also, while the phase change occurring *via* intercalation of Li into V_2O_5 is often observed to be homogeneous,^{14,16,20,34} the chemical lithiation of urea-combustion synthesized V_2O_5 leads to only partial formation of $\text{Li}_x\text{V}_2\text{O}_5$ phases at lower concentrations of Li. This could be possibly attributed to the room temperature lithiation and high electro-active surface area of urea combustion synthesized V_2O_5 , as opposed to bulk V_2O_5 powders. More importantly, reversibility of the Li intercalation into bare and chemically lithiated V_2O_5 phases at different stages were thoroughly explored. Intercalation of <0.5 Li into the V_2O_5 structure (forming $\epsilon\text{-Li}_{0.5}\text{V}_2\text{O}_5$) is considered to be highly reversible, whereas further intercalation ($0.5 < x < 1.0$) leads to the formation of $\delta\text{-LiV}_2\text{O}_5$ phase which is also reversible and evident from the electrochemical extraction of Li in $\text{Li}0.2$ and $\text{Li}0.5$. Intercalation of higher concentration of Li to attain $\gamma\text{-Li}_2\text{V}_2\text{O}_5$ (Li_2) and $\omega\text{-Li}_{2.5}\text{V}_2\text{O}_5$ (Li_3) phases results in the formation of irreversible phases with highly distorted crystal structure. The transition from γ to $\omega\text{-Li}_x\text{V}_2\text{O}_5$ phases results in amorphization as observed in Li_2 (equivalent to electrochemical discharge to $< 2.0 \text{ V}$ vs. Li), which has never been reported to the best of our knowledge. Interestingly, at 3 moles of BuLi concentration (Li_3), accommodation of 2.5 moles of Li per formula unit *via* the chemical route has similar charge-discharge profiles to that of the subsequent cycles of bare V_2O_5 . Intercalation of such large amount of Li enables the formation of irreversible $\omega\text{-Li}_x\text{V}_2\text{O}_5$ phase and it is observed from the second cycle onwards that this pre-insertion enabled better cycleability compared to bare V_2O_5 .

In the electrochemical lithiation, the reaction happened in a short period of time (hours), whereas chemical lithiation occurred over a longer period of time (days), which may provide a reason for the poor structural stability of V_2O_5 during electrochemical studies, and indeed, the effect of different durations cannot be ruled out. Finally, it must be taken into account that the layered structure of V_2O_5 and multiple oxidation states of vanadium enables accommodation of a variety of ions such as Li, Cu, Mg, Ag, Al and water molecules in between the interlayer spacing.^{12,39–50} The presence of small amounts of impurities (dopants) could drastically influence the electrochemical behavior of V_2O_5 cathodes and this provides the reason in which such pre-lithiated/doped electrodes delivered stable capacity after the first few initial cycles compared to native phase. Another way to improve the cycleability is restricting the electrochemical lithiation to one mole, unfortunately such restriction certainly provides less specific capacity ($\sim 147 \text{ mAh g}^{-1}$); nevertheless, in this case the amorphization of the V_2O_5 layered structure can be prevented. Surprisingly, compatibility of the electrochemically-lithiated V_2O_5 phase is found to be poor toward $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes and it is clearly evident from the cycling profiles of $\text{LiV}_2\text{O}_5/\text{Li}_4\text{Ti}_5\text{O}_{12}$ full-cell. Further studies are in progress to improve the cycleability of the V_2O_5 cathodes especially in full-cell configuration by adopting interlayer doping with other metals and carbon coating etc.

Conclusions

Sub-micron sized V_2O_5 powders were synthesized by urea combustion method and chemically lithiated using butyl lithium. The effects of lithium intercalation on the layered structure of V_2O_5 were studied with various concentrations of Li. Increasing the concentration of chemical lithiation into V_2O_5 structure results in the structural collapse especially at 2 moles of BuLi concentration, observed via XRD, whereas during electrochemical discharge this structure could be further reformed into irreversible ω - $Li_xV_2O_5$ phase. XPS and ICP analyses were carried out to confirm the presence and elucidate the amount of Li present in each of the chemically-lithiated compounds. Electrochemical studies evidenced the irreversibility of chemically lithiated phases when the BuLi concentration exceeds >1 mole per formula unit. Restricted electrochemical lithiation (via reduced voltage range) was carried out to compare the performance among chemically-lithiated phases. Furthermore, full-cell configuration was assembled and demonstrated for electrochemically lithiated V_2O_5 cathode with $Li_4Ti_5O_{12}$ anode for the first time.

Acknowledgments

This work was supported by funding from Competitive Research Program (CRP) (Grant no. NRF-CRP4-2008-03) and Clean Energy Research Project (CERP) (Grant no. NRF-2009-EWT-CERP001-036). Authors acknowledge Timcal for gratis providing Super PTM Li Carbon black. The electron microscopy was performed at the Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang Technological University, Singapore. The authors also acknowledge the help of Prof. Richard Webster and Dr. Bahareh Khezri for inductively-coupled plasma (ICP) analyses and Chow Shiau Kee for her aid in X-ray photoelectron spectroscopy (XPS) data collection.

References

1. V. Aravindan, J. Gnanaraj, Y.-S. Lee, and S. Madhavi, *Journal of Materials Chemistry A*, **1**, 3518 (2013).
2. N.-S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, and P. G. Bruce, *Angew. Chem., Int. Ed.*, **51**, 9994 (2012).
3. C. M. Hayner, X. Zhao, and H. H. Kung, *Annu. Rev. Chem. Biomol. Eng.*, **3**, 445 (2012).
4. M. M. Thackeray, C. Wolverton, and E. D. Isaacs, *Energy Environ. Sci.*, **5**, 7854 (2012).
5. E. J. Cairns and P. Albertus, *Annu. Rev. Chem. Biomol. Eng.*, **1**, 299 (2010).
6. Y. L. Cheah, V. Aravindan, and S. Madhavi, *J. Electrochem. Soc.*, **159**, A273-A280 (2012).
7. Y. L. Cheah, V. Aravindan, and S. Madhavi, *ACS Appl. Mater. Interfaces*, **4**, 3270 (2012).
8. Y. L. Cheah, N. Gupta, S. S. Pramana, V. Aravindan, G. Wee, and M. Srinivasan, *J. Power Sources*, **196**, 6465 (2011).
9. Y. L. Cheah, R. von Hagen, V. Aravindan, R. Fiz, S. Mathur, and S. Madhavi, *Nano Energy*, **2**, 57 (2013).
10. R. Pitchai, S. Shivakumara, H. N. Vasan, and N. Munichandraiah, *J. Phys. Chem. C*, **112**, 16700 (2008).
11. R. Pitchai, V. Thavasi, S. G. Mhaisalkar, and S. Ramakrishna, *J. Mater. Chem.*, **21**, 11040 (2011).
12. C. M. Ban, N. A. Chernova, and M. S. Whittingham, *Electrochem. Commun.*, **11**, 522 (2009).
13. C. M. Ban and M. S. Whittingham, *Solid State Ionics*, **179**, 1721 (2008).
14. B. Pecquenard, D. Gourier, and N. Baffier, *Solid State Ionics*, **78**, 287 (1995).
15. E. Prouzet, C. C. d. Moulin, F. Villian, and A. Tranchant, *Faraday Trans.*, **92**, 103 (1996).
16. K. West, B. Zachau-Christiansen, T. Jacobsen, and S. Skarup, *Solid State Ionics*, **76**, 15 (1995).
17. R. J. Cava, A. Santoro, D. W. Murphy, S. M. Zahurak, R. M. Fleming, P. Marsh, and R. S. Roth, *J. Solid State Chem.*, **65**, 63 (1986).
18. J. M. Cocciantelli, P. Gravereau, J. P. Doumerc, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.*, **93**, 497 (1991).
19. J. M. Cocciantelli, M. Menetrier, C. Delmas, J. P. Doumerc, M. Pouchard, and P. Hagenmuller, *Solid State Ionics*, **50**, 99 (1992).
20. C. Delmas, S. Brethes, and M. Menetrier, *J. Power Sources*, **34**, 113 (1991).
21. C. Delmas, H. Cognac-Auradou, J. M. Cocciantelli, M. Menetrier, and J. P. Doumerc, *Solid State Ionics*, **69**, 257 (1994).
22. H. Katze, M. Czank, W. Depemir, and S. S. v., *Philosophical Magazine Part B*, **75**, 757 (1997).
23. D. W. Murphy, P. A. Christian, F. J. Disalvo, and J. V. Waszczak, *Inorg. Chem.*, **18**, 2800 (1979).
24. P. Rozier, J. M. Savariault, and J. Galy, *Solid State Ionics*, **98**, 133 (1997).
25. J. M. Savariault and P. Rozier, *Physica B*, **234-236**, 97 (1997).
26. M. S. Whittingham and M. B. Dines, *J. Electrochem. Soc.*, **124**, 1387 (1977).
27. B. Garcia, M. Millet, J. P. Pereira-Ramos, N. Baffier, and D. Bloch, *J. Power Sources*, **81**, 670 (1999).
28. J. M. Cocciantelli, J. P. Doumerc, M. Pouchard, M. Broussely, and J. Labat, *J. Power Sources*, **34**, 103 (1991).
29. M. Eguchi and K. Ozawa, *Electrochim. Acta*, **52**, 2657 (2007).
30. C. Leger, S. Bach, P. Soudan, and J. P. P. Ramos, *J. Electrochem. Soc.*, **152**, A236-A241 (2005).
31. L. Q. Mai, L. Xu, B. Hu, and Y. H. Gu, *J. Mater. Res.*, **25**, 1413 (2010).
32. B. Y. Liaw, I. D. Raistrick, and R. A. Huggins, *Solid State Ionics*, **45**, 323 (1991).
33. E. A. Meulenkamp, v. K. W., and A. R. Schlattmann, *Solid State Ionics*, **126**, 235 (1999).
34. J. M. Cocciantelli, M. Menetrier, C. Delmas, J. P. Doumerc, M. Pouchard, M. Broussely, and J. Labat, *Solid State Ionics*, **78**, 143 (1995).
35. A. Q. Pan, J. G. Zhang, Z. M. Nie, G. Z. Cao, B. W. Arey, G. S. Li, S. Q. Liang, and J. Liu, *J. Mater. Chem.*, **20**, 9193 (2010).
36. S. Wang, Z. Lu, D. Wang, C. Li, C. Chen, and Y. Yin, *J. Mater. Chem.*, **21**, 6365 (2011).
37. C. D. Wagner, A. V. Naumkin, A. Kraut-Vass, J. W. Allison, C. J. Powell, J. John, R. Rumble, and R. NIST X-ray photoelectron spectroscopy database in, Database 20, Version 3.5 ed. (2003).
38. Y. L. Cheah, V. Aravindan, and S. Madhavi, *ACS Applied Materials & Interfaces*, **5**, 3475 (2013).
39. D. Imamura and M. Miyayama, *Solid State Ionics*, **161**, 173 (2003).
40. S. Kittaka, S. Takahara, T. Yamaguchi, and M. C. B. Funel, *Langmuir*, **21**, 1389 (2005).
41. C. V. S. Reddy, A.-P. Jin, X. Han, Q.-Y. Zhu, L.-Q. Mai, and W. Chen, *Electrochem. Commun.*, **8**, 279 (2006).
42. C. V. S. Reddy, J. Wei, Z. Quan-Yao, D. Zhi-Rong, C. Wen, S.-i. Mho, and R. R. Kalluru, *J. Power Sources*, **166**, 244 (2007).
43. A. Sakunthala, M. V. Reddy, S. Selvakarapandian, B. V. R. Chowdari, and P. C. Selvin, *Energy Environ. Sci.*, **4**, 1712 (2011).
44. Y. Wei, C.-W. Ryu, and K.-B. Kim, *J. Power Sources*, **165**, 386 (2007).
45. Y. Wei, C.-W. Ryu, and K.-B. Kim, *J. Alloys Compd.*, **459**, L13-L17 (2008).
46. T. Yao, Y. Oka, and N. Yamamoto, *J. Mater. Chem.*, **2**, 331 (1992).
47. S. Zhan, C. Wang, G. Chen, F. Du, and Y. Wei, *Ionics*, **16**, 209 (2010).
48. S. Zhan, Y. Wei, X. Bie, C. Wang, F. Du, G. Chen, and F. Hu, *J. Alloys Compd.*, **502**, 92 (2010).
49. S. Y. Zhan, G. Chen, D. L. Liu, A. Li, C. Z. Wang, and Y. J. Wei, *J. Alloys Compd.*, **479**, 652 (2009).
50. S. Y. Zhan, C. Z. Wang, K. Nikolowski, H. Ehrenberg, G. Chen, and Y. J. Wei, *Solid State Ionics*, **180**, 1198 (2009).