



## Review

# Synthesis and electrochemical properties of vanadium oxide materials and structures as Li-ion battery positive electrodes



David McNulty<sup>a, b</sup>, D. Noel Buckley<sup>a, b, c</sup>, Colm O'Dwyer<sup>c, d, e, \*</sup>

<sup>a</sup> Department of Physics and Energy, University of Limerick, Limerick, Ireland

<sup>b</sup> Charles Parsons Initiative on Energy and Sustainable Environment, University of Limerick, Limerick, Ireland

<sup>c</sup> Materials & Surface Science Institute, University of Limerick, Limerick, Ireland

<sup>d</sup> Department of Chemistry, University College Cork, Cork, Ireland

<sup>e</sup> Micro & Nanoelectronics Centre, Tyndall National Institute, Lee Maltings, Cork, Ireland

## HIGHLIGHTS

- Full scope review of the synthesis of vanadium oxide and related phases.
- A wide ranging summary of shape and size control of vanadium oxide phases.
- Electrochemical performances of vanadium oxides as Li-ion battery electrodes.

## ARTICLE INFO

## Article history:

Received 2 April 2014

Received in revised form

15 May 2014

Accepted 22 May 2014

Available online 20 June 2014

## Keywords:

Li-ion batteries

Vanadium oxide

Nanomaterials

Electrochemistry

Energy storage

## ABSTRACT

The electrochemical intercalation of lithium into vanadium pentoxide was first reported in the 1970's. Over the last 40 years vanadium oxides have continued to be the subject of much research due to their desirable physical properties. Initial results with bulk  $V_2O_5$  and  $V_2O_5$  gels demonstrated the potential for application as a cathode material for lithium batteries. Encouraging specific capacities exceeding  $250 \text{ mAh g}^{-1}$  were accompanied by severe capacity fading, which prevented widespread commercial application of  $V_2O_5$ -containing cathodes. Following the commercial release of the Li-ion battery, the development of layered materials that reversibly intercalated lithium, and the resurgence in nanoscale materials for Li-ion and alternative batteries, have opened new opportunities for the examination of the influence of material structure on cell performance. Recent decades have witnessed advances in the control of shape, structure and function of Li-ion battery materials. This review details the synthesis and structural properties of vanadium oxides, one of the model layered battery materials, and reviews the synthesis and structure of vanadium oxides and related polymorphs, bronzes and phases. Their electrochemical characteristics under a wide range of conditions are assessed and compared as positive electrode materials in lithium and lithium-ion batteries up to the present day.

© 2014 Elsevier B.V. All rights reserved.

## 1. From lithium batteries to lithium ion batteries

Lithium batteries have been investigated for decades as a means of meeting our energy storage goals. There are several reasons why lithium was initially investigated as an anode material. Lithium is the lightest and most electropositive metal ( $-3.04 \text{ V}$  vs. standard hydrogen electrode) [1]. The combination of these two characteristics results in lithium having a particularly favourable energy content, with a theoretical specific capacity of  $3860 \text{ mAh g}^{-1}$  in

comparison with  $820 \text{ mAh g}^{-1}$  for zinc and  $260 \text{ mAh g}^{-1}$  for lead [2]. The use of lithium in primary batteries was first investigated in the 1960's and 70's [3–5] however at that time aqueous electrolytes were being used. One of the first major issues which had to be overcome was the lack of a stable electrolyte medium for use with pure lithium. The practical use of lithium cells was not realised until after the development of suitable non-aqueous electrolytes. In an effort to improve the electrochemical performance of these cells, new electrolytes were extensively studied. Initially, various insertion compounds were investigated as cathode materials for lithium batteries [6,7]. These materials host lithium ions within their crystalline structures during a state of discharge and the lithium ions are removed during a state of charge. Ideally this is a reversible

\* Corresponding author. Department of Chemistry, University College Cork, Cork, Ireland. Tel.: +353 (0) 21 4902732; fax: +353 (0) 21 4274097.

E-mail address: [c.odwyer@ucc.ie](mailto:c.odwyer@ucc.ie) (C. O'Dwyer).

reaction without any major phase changes to the cathode material. While these insertion compounds were being investigated as cathode materials, pure lithium was being used as the anode material. Problems associated with lithium corrosion and the formation of lithium dendrites within the cathode material were a cause for concern [8–11]. These issues resulted in poor cycling efficiency and shortened cycle life. It became clear that it was necessary to replace the lithium metal with a lithium containing compound.

Initially lithium alloys with other metals such as aluminium and tin were investigated for this purpose [12]. However, it was found that they suffer from severe morphological changes upon cycling due to large volume changes [13]. The electrochemical insertion of lithium into graphite was also investigated [14], however severe problems due to exfoliation were encountered [15]. These issues lead to the development of the “rocking chair” concept. The concept was first reported by Lazzari et al. in 1980 [16] and named by Armand [17]. It involves using two insertion compounds based on metallic oxides or sulfides as electrodes. The system described was a  $\text{Li}_x\text{WO}_2/\text{Li}_y\text{TiS}_2$  cell, with an average cell voltage of 1.8 V. One of the electrodes has to have been previously lithiated (in this case  $\text{WO}_2$ ), this electrode acts as the main source of lithium in the cell and hence solves the issues associated with using pure lithium. While this method did represent an alternative to using pure lithium, the cell had a low energy density. Thus it was not very attractive for practical use. Over the years the “rocking chair” system has been called various names including the shuttlecock [18] and swing electrode system [19]. Today these types of batteries are simply called lithium ion batteries. The real breakthrough for lithium ion batteries came in the 1980's when disordered carbon was identified as good candidate as an anode material and  $\text{Li}_x\text{CoO}_2$  was identified as a suitable cathode material [20]. In 1990, Nagura announced the commercial availability of the first lithium ion battery based on a carbon (non-graphitic) anode and a  $\text{LiMnO}_2$  cathode [21]. The electrochemical performance of these materials and their alternatives will now be discussed.

## 2. Cathode materials for lithium ion batteries

The capacity of lithium ion batteries is typically limited by the cathode. Therefore it is necessary to improve the capacity of the cathode in order to improve the performance of lithium ion batteries. It is for this reason that there is such a tremendous interest in developing enhanced cathode materials. As mentioned above insertion materials were quickly identified as suitable compounds for use as cathode materials. The first materials which were investigated were the chalcogenides [22].  $\text{TiS}_2$  has been extensively studied due to its stable layer structure and electronic conductivity [23,24]. In fact  $\text{TiS}_2$  was used as the cathode material in the first commercial lithium battery with  $\text{LiAl}$  as the anode material [25]. The battery was a coin cell for watches. While suitable for applications such as watch batteries these cells were not practical for larger devices. Following on from the chalcogenides, a lot of attention was given to metal oxides. Initial research focused on metal oxides such as oxides of molybdenum [26,27], tungsten [28], vanadium [29], chromium [30] and manganese [31]. The possible use of  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x\text{NiO}_2$  was first reported by Mizushima et al. in 1980 [32,33] and following on from improvements in non-aqueous electrolytes these compounds quickly became the most studied insertion materials for use as cathodes.

### 2.1. Lithium nickel oxide ( $\text{Li}_x\text{NiO}_2$ ) and lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ )

The theoretical specific capacity of  $\text{Li}_x\text{NiO}_2$  assuming 1 Li per  $\text{NiO}_2$  may be removed is  $\approx 275 \text{ mAh g}^{-1}$ , however a lower capacity is

obtained in actual test cells [34].  $\text{Li}_x\text{NiO}_2$  was reported to have a larger initial specific capacity than  $\text{Li}_x\text{CoO}_2$ , having values up to  $\approx 200 \text{ mAh g}^{-1}$  compared to  $\approx 150 \text{ mAh g}^{-1}$  obtained for  $\text{Li}_x\text{CoO}_2$ , as can be seen in Fig. 1 [25]. However, there are several reasons why this insertion compound has not received much practical use. The synthesis of  $\text{Li}_x\text{NiO}_2$  is much more difficult than  $\text{Li}_x\text{CoO}_2$  due to the formation of a nickel over-stoichiometric phase [35,36]. Capacity fading is a severe issue for  $\text{Li}_x\text{NiO}_2$  [37,38] and also the thermal stability of  $\text{Li}_x\text{NiO}_2$  is much lower than for other materials such as  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x\text{Mn}_2\text{O}_4$  [39,40]. It was reported that the cycle life of  $\text{Li}_x\text{NiO}_2$  cells is strongly dependent on the depth of discharge [41]. When the specific capacity was restricted to  $\approx 90 \text{ mAh g}^{-1}$ , a cycle life of 200 cycles was reported. However, when the specific capacity was restricted to 130 and  $200 \text{ mAh g}^{-1}$  cycle lives of 98 and 12 cycles respectively were reported. This poor performance for deeper discharges is due to the formation of irreversible phases due to increased concentrations of lithium in  $\text{NiO}_2$  [42]. The electrochemical performance of  $\text{Li}_x\text{NiO}_2$  can be improved by partial substitution of Ni with other metals such as cobalt and magnesium. Even low amounts (>10%) of these metals can significantly improve the capacity fading issues. This improvement in cycling ability is due to the suppression of phase transitions which are observed for  $\text{Li}_x\text{NiO}_2$ .

The performance of three dimensional spinel lithium manganese oxide has been the subject of a tremendous amount of research [43–46]. There are many advantages to using manganese over other materials such as cobalt and nickel including its lower cost and increased thermal stability [47]. However, electrochemically  $\text{Li}_x\text{Mn}_2\text{O}_4$  does not perform as well as the mentioned cobalt and nickel oxides. The theoretical specific capacity of  $\text{Li}_x\text{Mn}_2\text{O}_4$ , with  $x = 1$ , is  $\approx 148 \text{ mAh g}^{-1}$ , experimentally this value is found to be closer to  $\approx 120 \text{ mAh g}^{-1}$ , as shown in Fig. 1 [34].  $\text{Li}_x\text{Mn}_2\text{O}_4$  suffers from severe capacity fading [46,48]. It has been reported that the capacity fading issues are strongly reduced when  $\text{Li}_x\text{Mn}_2\text{O}_4$  is over lithiated to a  $\text{Li}_{(1+\delta)}\text{Mn}_{(2-\delta)}\text{O}_4$  composition [49]. Orthorhombic  $\text{Li}_x\text{MnO}_4$  has also been investigated, due to its higher theoretical specific capacity than  $\text{Li}_x\text{Mn}_2\text{O}_4$ , however it has been reported that there is a gradual structural transformation during battery operation and after a few cycles the material behaves very much like  $\text{Li}_x\text{Mn}_2\text{O}_4$  [50,51].

### 2.2. Lithium cobalt oxide ( $\text{Li}_x\text{CoO}_2$ )

Lithium cobalt oxide is the most commonly used cathode material in lithium ion batteries today [1,2,52,53]. There are several

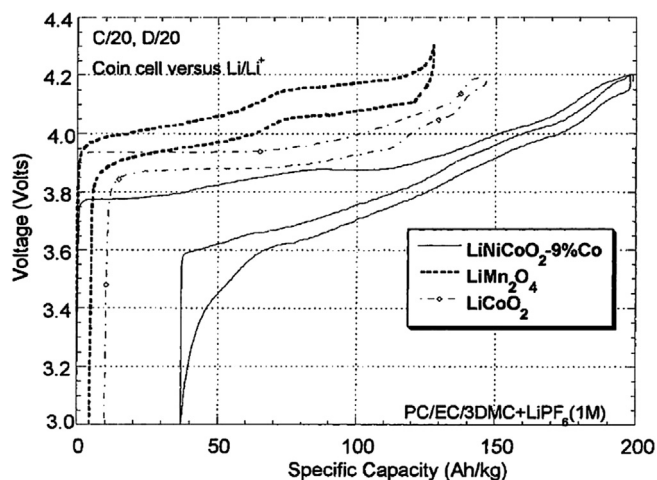


Fig. 1. Specific capacity for the first discharge and charge for  $\text{LiNiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$  [25].

Download English Version:

<https://daneshyari.com/en/article/1286569>

Download Persian Version:

<https://daneshyari.com/article/1286569>

[Daneshyari.com](https://daneshyari.com)