

## Stable cycling of thin-film vanadium oxide electrodes between 4 and 0 V in lithium batteries

Ping Liu\*, Se-Hee Lee, C. Edwin Tracy, John A. Turner

National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA

### Abstract

Vanadium oxide prepared by plasma-enhanced chemical vapor deposition was cycled in different voltage ranges in a lithium battery. Electrochemical cycling results show a surprisingly low irreversibility during the first discharge and good stability for close to 1000 cycles between 4 and 0 V. Raman spectroscopy results indicate that a major structural transformation takes place when the films are cycled down to 1.8 V, after which the structural features remain intact even after cycling to 0 V. Degradation of the electrode only occurs after extended cycling.

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*Keywords:* Vanadium oxide; Raman spectra; Lithium insertion; Cycling stability; Anode material

### 1. Introduction

The reversible insertion of lithium ions into host materials such as metal oxides and carbonaceous materials serves as the basic principle of today's lithium-ion technology [1]. Much research has been devoted to understanding the structure–property relationship for a wide variety of metal oxides. It is well known that homogeneous topotactic reaction only takes place in certain a composition range, beyond which phase transitions occur. For example, crystalline vanadium oxide undergoes a series of phase transitions as the amount of lithium increases. Insertion of 3 moles of lithium into  $V_2O_5$  results in the formation of  $\omega$ - $Li_3V_2O_5$ , which has a sodium chloride type cubic structure and is found to be reversible [2]. Since this rock-salt structure does not have any vacancies to accommodate any more lithium, the  $\omega$ - $Li_3V_2O_5$  composition is considered to be the limit of the Li–V–O system.

Recently,  $LiMVO_4$  ( $M = Zn, Cd, Ni$ ), and amorphous compounds such as  $RVO_4$  ( $R = In, Fe$ ) and  $MV_2O_{6+\delta}$  ( $M = Fe, Mn, Co$ ) [3–5], molybdates [6,7], and 3d-metal oxides [8–11] have been investigated as higher-capacity alternatives to carbon anode materials in lithium-ion batteries. Initial charge capacities as high as 1300 mAh/g have been reported for  $FeVO_4 \cdot 2.7H_2O$ , although the capacity quickly fades during cycling (61% of initial capacity retained

after 10 cycles) [4]. The exact reaction mechanism is still a matter of debate. NMR and XAS analyses performed on deeply discharged  $Na_{0.25}MoO_3$  indicate the formation of a lithium oxide-like compound as well as a Li–Mo–O. Upon subsequent charging, the decomposition of “lithium oxide” seems to contribute to the reversible capacity [6,7].

Very recently, Ali et al. demonstrated that thin-film  $Ni_2V_2O_5$  electrodes exhibit improved kinetics and cyclability compared to bulk materials [12]. We present our results on lithium insertion into amorphous vanadium oxide thin-film electrodes between 0 and 4 V. Our observations include a highly reversible cycling in this voltage range. Raman spectra of deeply discharged vanadium oxide thin films indicate dramatic structural changes between 1.5 and 1.8 V, after which the structural features remain largely intact. To our knowledge, this work represents the first investigation and analyses of extended cyclability data (nearly 1000 cycles) on deeply discharged metal oxide thin films.

### 2. Experimental

Vanadium oxide thin-film electrodes were prepared by plasma-enhanced chemical vapor deposition as described in a previous publication [13]. The vanadium source,  $VOCl_3$ , was controlled at 10 °C and carried to the reaction chamber by argon at a pressure of 15 psi. The flow rates of  $VOCl_3/Ar$ ,  $H_2$ ,  $O_2$  were controlled at 500, 28 and 15 sccm, respectively.

\* Corresponding author. Tel.: +1-303-384-6503; fax: +1-303-384-6655.  
E-mail address: [pliu@nrel.gov](mailto:pliu@nrel.gov) (P. Liu).

The temperature of the substrate, 430 stainless steel, was 25 °C. A 10 min deposition resulted in a film thickness of approximately 0.6  $\mu\text{m}$ , as measured by a Tencor profilometer. For evaluation of the film in a lithium battery, a three-electrode cell was used with lithium metal as both the counter and reference electrodes, while a solution of 1 M  $\text{LiClO}_4$  in propylene carbonate was used as the electrolyte. Charge and discharge experiments were performed utilizing an Arbin battery testing system (Arbin Instruments, TX, USA) at a current density of 50  $\mu\text{A}/\text{cm}^2$ . To investigate the structural changes during electrochemical cycling, Raman spectra were collected on samples which were cycled between different voltage ranges. The spectra were taken in the quasi-backscattering geometry using 100 mW of the 514.5 nm line of an Ar ion laser (focused to a line of 5 mm  $\times$  100  $\mu\text{m}$ ) as the excitation source. The signal was dispersed by a Spex 0.6 m triple spectrometer and detected with a liquid-nitrogen-cooled high-resolution charge-coupled-device detector array. Both the spectral resolution and the accuracy in the Raman shift are estimated to be  $\sim 2 \text{ cm}^{-1}$ .

### 3. Results and discussion

Fig. 1 presents the capacity cycling data of a 0.6  $\mu\text{m}$  thick PECVD vanadium oxide electrode in two different voltage ranges (4–1.5 and 4–0 V). The initial 15 cycles were performed between 4 and 1.5 V. Consistent with previously reported results [13], the electrode delivers a reversible capacity of 70  $\mu\text{Ah}/(\mu\text{m}^2)$ . Since the PECVD vanadium oxide has a density of 3  $\text{g}/\text{cm}^3$ , this volume capacity translates to 233  $\text{mAh}/\text{g}$ . The cycling range was subsequently expanded to 0 V. An initial capacity of over 140  $\mu\text{Ah}/(\mu\text{m}^2)$  is obtained, which gradually increases over the next 38 cycles. When the range is switched back to 4–1.5 V, the initial capacity is restored and stable cycling is achieved. This restoration demonstrates that any structural transformation which occurs during cycling down to 0 V

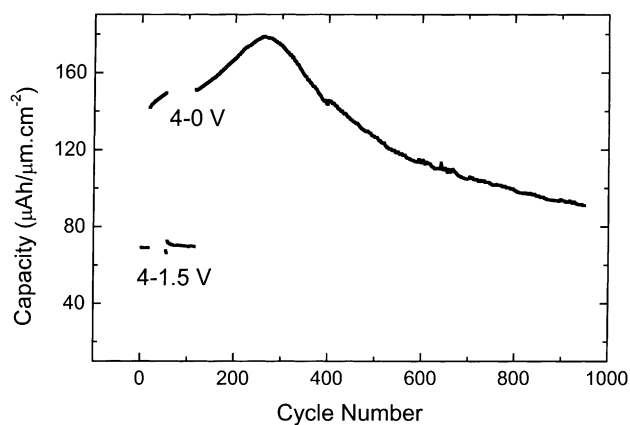


Fig. 1. The charge capacity cycling data of a PECVD vanadium oxide thin-film electrode between different voltage ranges.

does not compromise the material's ability to function as a reversible lithium battery cathode.

We then again switched the cycling range back to 4–0 V for an extended life test. Surprisingly, the capacity continues to increase as cycling proceeds for another 150 cycles when the capacity reaches  $\sim 180 \mu\text{Ah}/(\mu\text{m}^2)$ . A similar capacity increase with cycling has been observed in the case of copper oxide but the reason remains unknown [11]. The volumetric capacity data translate to a mass capacity of 600  $\text{mAh}/\text{g}$  and a composition of  $\text{Li}_{4.1}\text{V}_2\text{O}_5$ . The capacity then gradually degrades to about 50% of the highest value by the end of the test, the 950th cycle. To the best of our knowledge, this is the first time that vanadium oxide has been cycled over this potential range for such extended period of time. In comparison, a survey of the literature reveals that the  $R_{10/1}$  value (which represents the charge capacity retention after 10 cycles) ranges from 0.85 for  $\text{Na}_{0.25}\text{MoO}_3$  to 0.61 for  $\text{FeVO}_4 \cdot 2.7\text{H}_2\text{O}$  [4]. Data of up to 100 cycles have been reported for  $\text{Na}_{0.25}\text{MoO}_3$  when the capacity retention was approximately 50% [6].

The first and second cycle charge–discharge curves for vanadium oxide are presented in Fig. 2. During the first discharge, the curve is largely featureless down to 1.5 V, which is consistent with previous results [13]. The profile remains featureless down to approximately 0.2 V after which a flat region is observed (0–0.2 V). It is known that when electrodes are discharged to potentials close to that of  $\text{Li}/\text{Li}^+$ , the decomposition of electrolyte and the formation of a solid electrolyte interface (SEI) layer take place, which usually gives rise to a large irreversible capacity. Another reaction, the decomposition of the oxide framework along with the possible formation of lithium oxide, may also contribute to the irreversibility. Indeed, irreversibility ranging from 23 to 45% has been reported for various oxides [6]. Our PECVD vanadium oxide, when cycled between 4 and 0 V, has an irreversibility of 17%. This is somewhat surprising, since the irreversibility is over 30% when the electrode is cycled between 4 and 1.5 V at similar current densities. This irreversibility is well documented and may be

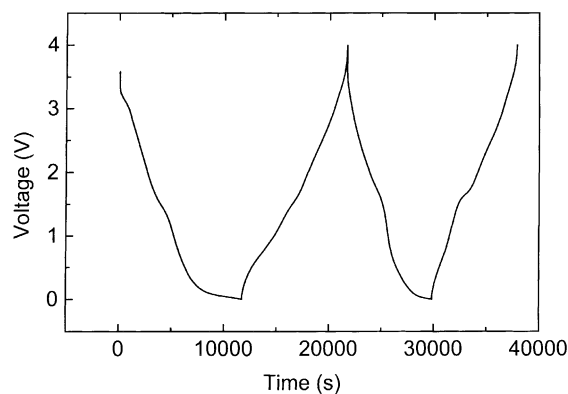


Fig. 2. The charge–discharge curves of a PECVD vanadium oxide thin-film electrode for the first and second cycles.

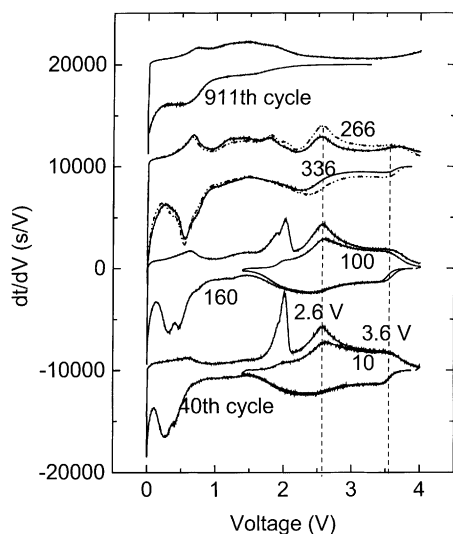


Fig. 3. The differential plots of the charge–discharge data for different cycles.

attributed to the entrapment of  $\text{Li}^+$  in the cathode [14,15]. The fact that cycling the electrode down to 0 V improves the Coulomb efficiency indicates that the contribution from the formation of the SEI layer is minimal.

The structural transformation during extended cycling (Fig. 1) can be elucidated by the differential charge–discharge curves shown in Fig. 3. When cycled between 4 and 1.5 V, two pairs of broad features are visible at approximately 3.6 and 2.6 V, respectively. The largely symmetric redox peaks are indicative of highly reversible processes. These features remain intact even after cycling down to 0 V for over 20 cycles as shown by the profile of the 40th cycle. An additional peak is observed at around 0.25 V. On the charging curve, a strong oxidation peak is visible at around 2 V. It is reasonable to assign the peak as the oxidation process for the reduction peak at 0.25 V. Such a large hysteresis is consistent with the mechanism proposed in the literature for metal oxide reduction at very low potentials, which involves the formation of lithium oxide and metal and/or metal suboxide [3,4,6,16]. Charging the electrode to 4 V appears to fully restore the original vanadium oxide composition, since the profile of 100th cycle (which was obtained between 4 and 1.5 V) is identical to that of the 10th cycle.

Again in Fig. 3, the retention of the charge–discharge profiles in the 4–1.5 V region is still evident up to 266 cycles, before the overall capacity starts to degrade. By the 336th cycle, the capacity has degraded from the largest value of  $180 \mu\text{Ah}/(\mu\text{m}^2)$  in Fig. 1. A comparison of the profiles of the 266th and 336th cycles reveals that degradation of capacity mainly takes place in the high voltage region, while the profile between 0 and 1.5 V is largely unchanged. After extended cycling out to 911 cycles, the reversible capacity in the high voltage region becomes negligible, while the capacity in low voltage region (between 2 and 0 V) has degraded to a much lesser extent.

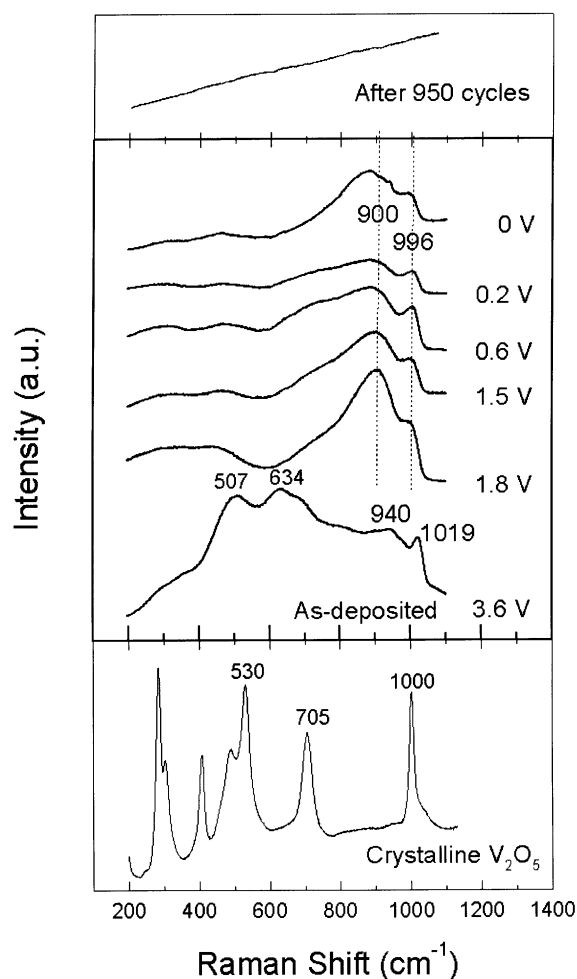


Fig. 4. Raman spectra of vanadium oxide electrodes cycled between 4 V and different lower voltage limits. Samples were pre-cycled five times before the spectra were taken. The comparison spectra for a crystalline  $\text{V}_2\text{O}_5$  film, as well as an as-deposited film cycled for 950 cycles between 4 and 0 V, are also included.

To probe the structural changes during electrochemical cycling, Raman spectra were collected on  $\text{V}_2\text{O}_5$  samples which were cycled between different voltage ranges (Fig. 4). All cycling is stopped at the end of a charging process. The spectrum of a crystalline vanadium oxide thin film is also included for reference. The as-deposited PECVD vanadium oxide is amorphous as confirmed by X-ray diffraction measurements, which corroborates with its Raman spectrum. Only a few broad features are visible. The peak at  $1019 \text{ cm}^{-1}$  of the as-deposited film can be attributed to the  $\text{V(V)=O}$  vibration mode while that at  $940 \text{ cm}^{-1}$  corresponds to the  $\text{V(IV)=O}$  vibration mode. Crystalline vanadium oxide has a layered structure with each layer built up from  $\text{VO}_5$  pyramids sharing edges and corners. Within the  $\text{VO}_5$  pyramid, a very short  $\text{V=O}$  bond is observed, which gives rise to the strong peak at around  $1000 \text{ cm}^{-1}$ . The broad bands at  $507$  and  $634 \text{ cm}^{-1}$  for the PECVD film may be related to the bands at  $530$  and  $705 \text{ cm}^{-1}$ , respectively, which are observed in crystalline vanadium oxide. These bands are due to the

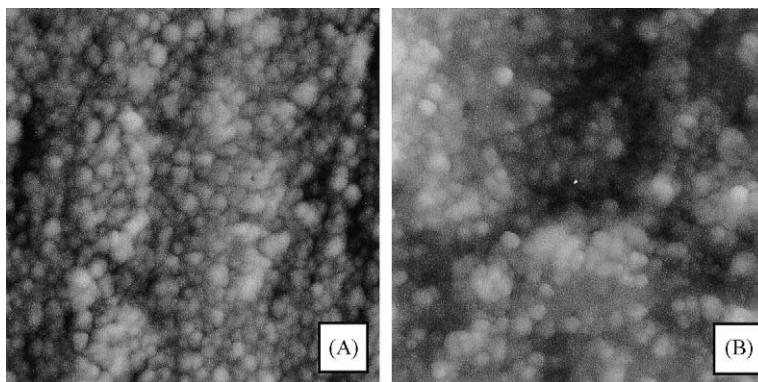


Fig. 5. AFM pictures of an as-prepared vanadium oxide thin film (A) on a stainless steel substrate and the same sample (B) after being cycled between 4 and 0 V for five cycles. The size of each image is  $2\ \mu\text{m} \times 2\ \mu\text{m}$ .

stretching modes of V–O bonds. The presence of only these broad features in the as-deposited film indicates a lack of long range order.

Again from Fig. 4, cycling of the vanadium oxide electrode between 4 and 1.8 or 1.5 V results in substantial changes to the Raman spectra. The bands attributable to the V=O bonds at  $900$  and  $996\ \text{cm}^{-1}$  are still present while those of the V–O bonds at  $507$  and  $634\ \text{cm}^{-1}$  have disappeared. The peak attributable to the V(IV)=O vibration at  $900\ \text{cm}^{-1}$  is the most dominant feature which grows at the expense of the peak at  $996\ \text{cm}^{-1}$  (V(V)=O vibration). As the cycling range extends to lower voltages, the essential features of the peaks remain unchanged while the overall intensity of all the peaks gradually decreases. In addition, both peaks at  $900$  and  $996\ \text{cm}^{-1}$  are shifted to lower frequencies as the discharge limit extends to lower values. As vanadium oxide is cycled to lower voltages, more vanadium may be irreversibly reduced to its lower valence form such as V(IV). This phenomenon might explain the red shift of both peaks. The vibration frequency of either V(V)=O or V(IV)=O bonds is affected by their neighboring single bonds, such as in the configurations of V–O–V(V)=O or V–O–V(IV)=O. A lower valence state of the first V certainly will reduce the strength of V=O bonds and hence their vibration frequencies. We also measured the spectrum of the vanadium oxide film that had been cycled for 950 cycles. No discernable peaks are observed, indicating a complete disappearance of any local structural ordering previously present in the film.

Possible morphological changes which may occur during cycling were probed by atomic force microscopy (AFM). Fig. 5 compares the images of an as-prepared (A) and a vanadium oxide sample (B) after five cycles between 4 and 0 V. The size of each image is  $2\ \mu\text{m} \times 2\ \mu\text{m}$ . It is evident that after five cycles, the basic features of morphology remain intact. The films are composed of granular domains with considerable voids between them. Such a structure is beneficial to maintain the macroscopic integrity of the films. These voids may elastically accommodate any microstructural changes induced by lithium insertion and removal.

In summary, amorphous vanadium oxide thin-film electrodes prepared by PECVD exhibit very good cycling stability between 4 and 0 V. Cycling down to 0 V initially does not affect the film's reversible capacity at high voltage ranges (4–1.5 V). Capacity degradation only takes place after extended cycling, when the majority of the reversible capacity is observed at low potentials (between 2 and 0 V). Our Raman analyses indicate that subsequent to a major irreversible structural transformation after cycling between 4 and 1.8 V, extension of the lower cycling limit does not induce further significant irreversible change. This phenomenon may be responsible for its stable electrochemical performance.

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