

Performance of copper-doped V_2O_5 xerogel in coin cell assembly

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Abstract

Copper-doped, vanadium pentoxide xerogel is prepared through a simple sol–gel procedure, followed by heterogeneous doping and freeze-drying. Composite cathodes were formed by spray-coating a mixture of the Cu-doped material, carbon, and binder onto aluminum foils. The composite cathodes were studied in 2016 coin cells with lithium anodes and supported liquid electrolyte. The electrochemical performance of the doped material is excellent. Up to 2.2 mol of lithium per mol of doped V_2O_5 can be reversibly intercalated. The composite cathodes also showed very high intercalation rate performance and an excellent cyclability with no capacity fading over a few hundred cycles (> 450). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: V_2O_5 ; Xerogel; Copper vanadium oxide; Coin cell; Lithium/lithium-ion battery

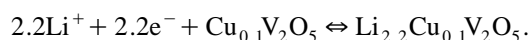
1. Introduction

Vanadium pentoxide gels have been studied over the past several decades and especially during the last two decades with the advent of sol–gel process techniques. It has been shown that the gels serve as host materials for a wide variety of metal cations. The large lithium insertion capacity of vanadium pentoxide gel-based cathodes, greater than two equivalents of lithium per vanadium [1–3], makes them attractive for use as cathodes in high capacity lithium batteries. Thin films or pellets of V_2O_5 xerogel material have been successfully used in lithium batteries with liquid or polymer electrolytes [4,5] as well as electrochromic electrodes and passive lithium reservoirs in electrochromic devices [6]. As thin films or powders, gel-based materials have been shown to intercalate larger amounts of lithium than does crystalline V_2O_5 [1–3,7].

In previous work in this laboratory, it was found that vanadium oxide hydrogels could be easily doped by a simple addition of a known amount of the doping metal. The reaction of silver metal with vanadium pentoxide hydrogel for example was found to be rapid at room temperature [8,9]. When the product was dried as a xerogel film or an aerogel-like powder [8,9], it supported highly

reversible Li^+ intercalation as well as highly reversible Ag^0 formation and reoxidation on repeated redox half cycles. The silver vanadium pentoxide formed in this way is amorphous and has higher conductivity than the parent V_2O_5 xerogel, and neither of these features is lost on repeated insertion/release cycles.

The characterization of gel based, copper-doped V_2O_5 materials has been reported earlier [10]. These materials maintain the layered structure typical of V_2O_5 with an increased electronic conductivity. As intercalation compounds, they are attractive options to use in lithium batteries because they can be fabricated by low cost processes, lithium insertion is reversible and a high experimental specific energy is achievable. The cathodes have a potential of around 3.7 V (vs. Li) at full charge and are able to intercalate a large number of lithium ions on a molar basis ($x > 2$ at full discharge for $Li_xCu_{0.1}V_2O_5$). This combination has resulted in an experimental specific energy exceeding 750 W h/kg for pellet electrodes of copper-doped V_2O_5 aerogels [10], corresponding to the cathodic reaction:



The specific capacity for this reaction is slightly larger than 300 A h/kg of active cathode material.

The present investigation is directed towards the performance of relatively thin composite cathodes containing the xerogel form of $Cu_{0.1}V_2O_5$. The cathodes are produced by

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a continuous, industrial-like process, with a practical loading in the range from 1 to 5 mA h/cm².

2. Experimental

The xerogel powders as well as the spray-coated cathodes were highly hygroscopic so that special precautions were required for preparing and handling the samples as well as for assembling the cells. In particular, the exposure to ambient (humid) air was avoided by handling all materials and cells in a dry room.

2.1. $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ preparation

The preparation of the copper-doped cathode is accomplished in three steps. Initially, vanadium pentoxide hydrogel was prepared by a sol gel route described elsewhere [11,12]. Briefly, a 0.5 M solution of sodium metavanadate (FLUKA, > 98%) was eluted through a column loaded with a proton exchange resin (Dowex 50 WX₂ 50–100 mesh). The effluent, a pale yellow solution of decavanadic acid, was collected in glass containers. A 1 day aging with no agitation resulted in the formation of a homogeneous vanadium pentoxide hydrogel.

The second step consisted in doping the V_2O_5 gel with copper. This was performed by mixing the selected stoichiometric amount of copper powder (ALFA 99.997% purity) with V_2O_5 hydrogel. The mixtures were vigorously blended until the copper powders were completely oxidized. X-ray measurements were performed on the dry doped materials. The absence of any peak associated with metallic copper was taken as evidence of complete reaction. Several preparations of doped- V_2O_5 hydrogel were made. They had the stoichiometry of $\text{Cu}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($n > 200$) and a consistency similar to the original, undoped V_2O_5 hydrogel.

Finally, dried $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel was obtained by freeze-drying the doped hydrogel under vacuum. After about 120 h in the freeze dryer, the sample was transferred in to a vacuum oven for the final drying step (12 h at 100°C and 10⁻³ Torr). With this procedure, the pore water and the physically bound water [13] were completely removed. The resulting red-brownish powder of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel contained only the strongly bonded water, 0.5 mol of H_2O per mol of V_2O_5 . The powder was then ball-milled and sieved (400 mesh) prior to any further use.

2.2. Spray-coated composite cathode preparation

First, the desired amount of binder (Kynar, ELF-Atochem) was dissolved in cyclopentanone by heating at 60°C for 1 h. Selected amounts of carbon (Ketjen black, AKZO NOBEL) and dry $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel were added into a blender to the Kynar/cyclopentanone solution, to obtain the desired weight ratio ($\text{Cu}_{0.1}\text{V}_2\text{O}_5$:KJB:Kynar =

80:10:10). After blending for 2 min, the slurry was spray-coated onto an aluminum foil (25 μm thick) by using an air brush (Badger mod. 350). Argon was used as propellant gas. The spray-coating operation was performed into a fume hood (solvent evaporation) located in a dry room (dry atmosphere, R.H. < 1%). The spray-coated samples were then dried at 60°C under vacuum for 12–18 h.

2.3. Cell fabrication and testing

The electrochemical characterization of the spray-coated electrodes was performed in a coin cell assembly. Spray-coated samples were cut in the form of discs for the cathodes (diameter: 14 mm; active material loading: 4 mg, active material thickness: 40 μm). The coin cells, containing the cathodes, were flooded with several drops of electrolyte and evacuated for several minutes until bubble evolution from the cathodes ceased. Two layers of separator (Celgard, Hoechst Celanese) impregnated with the electrolyte, were used to separate the cathode and the anode in the coin cells. The electrolyte was a 1 M solution of LiClO_4 (FLUKA, high purity dried at 170°C under vacuum) in propylene carbonate (Grant Chemicals, high purity, $\text{H}_2\text{O} < 20$ ppm). The electrolyte was impregnated into the separator by soaking for 24 h at 60°C. Lithium discs (Cyprus Foote) were manually pressed onto the coin cell lid. An X-MET (expanded metal net) disc was previously spot welded onto the coin cell lid to improve the electrical contact with the anode. Every cell contained an excess of lithium. Finally, the coin cell was sealed by crimping at 2 metric tons.

Galvanostatic charge/discharge tests were performed by using a battery cycler (Arbin Instruments, College Station, TX). Impedance measurements were performed by using a Frequency Response Analyzer (Solartron mod. 1260) coupled with a potentiostat (Solartron mod. 1287).

All experiments were performed at ambient temperature (22°C). The discharge rates (C/n) quoted later in this work are computed on the basis of the actual discharge time. The rate is given as the inverse of the discharge time (n). The specific capacity, energy and power are referred to the active material ($\text{Cu}_{0.1}\text{V}_2\text{O}_5$) weight. All spray-coated electrodes have the same area (1.54 cm²). The electrode active material loading ranged from 3 to 5 mg/cm².

3. Results and discussion

The reversibility of the lithium intercalation process in spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrodes in coin cell assembly was evaluated by means of coulometric titration. The experiment was performed by passing a current through the cell (13 mA/g) for a selected time (ca. 15000 s) that corresponded to the intercalation of about 0.4 equivalents of lithium. The intercalation steps were repeated until the cell hit the 1.5 V cut-off. As a final step the cell was

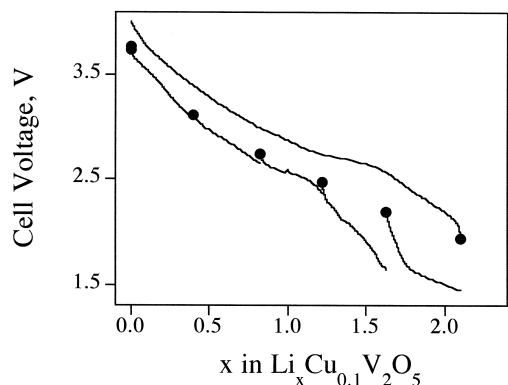


Fig. 1. Step discharge behavior of a spray coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in a coin cell assembly. The electrode quasi-equilibrium potential (V vs. Li) as a function of the amount of lithium intercalated by coulometric titration is also indicated (circles). Current density: 0.054 mA/cm^2 . Specific current: 13 mA/g . Active material loading: 4.1 mg/cm^2 .

recharged up to 4.0 V with the same current. After each step the cell was left at rest for 24 h to reach a quasi-equilibrium state prior to measuring the electrode potential. Fig. 1 illustrates the voltage behavior during the lithium insertion/release steps as well as the quasi-equilibrium electrode potential (QOCP, solid dots in the figure). The results clearly indicate the full reversibility of the intercalation process. More than two equivalents of lithium were inserted into the layered structure of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ and reversibly released in the following anodic polarization. The comparison between the QOCP and the cell voltage behavior during the current pulses gives important information about the intercalation process. Upon the insertion of the initial 1.2 equivalents of lithium per mole of active material, the cell did not show any substantial polarization. The cell voltage curves practically connect the QOCP points (see Fig. 1). This indicates the absence of any substantial diffusion or charge transfer limitation on the intercalation process. For further lithium insertion ($> 1.2 \text{ Li/V}_2$) the electrode polarization becomes important as indicated by the large difference of the cell voltage at the end of the pulse and the corresponding QOCP value. This behavior is typical of vanadium oxide xerogels [4]. It has been associated with the decrease of the diffusion coefficient of lithium in the solid phase of xerogel V_2O_5 [13]. Nevertheless, the copper doping reduces this effect [10] thus leaving the $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ cathodes able to deliver larger capacities than the parent V_2O_5 xerogel cathodes.

During the continuous lithium release step, the cell voltage remains within ca. 200 mV of the QOCP curve. After an initial quick rise, the cell voltage shows a plateau for a molar lithium composition of about 1.5 equivalents. Upon further release, the cell voltage tends to approach the QOCP. This behavior is in agreement with the proposed change in the lithium diffusion coefficient [13]. When the lithium ion concentration is decreased in the solid, its diffusion coefficient in the solid phase increases and this

allows for a faster release process. The final result is the achievement of the full reversibility of the lithium insertion process in spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$.

As a following test, the rate performance of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ spray-coated electrodes in a coin cell assembly were investigated. Fig. 2 shows the voltage vs. specific capacity curves obtained by discharging a cell at different current densities. The curves are mostly smooth throughout the whole discharge process, but especially at the lower current densities, they show three different electrode voltage slope regions. This behavior has been reported earlier for silver- and copper-doped V_2O_5 aerogel like materials [10]. In the high voltage region, $V > 2.7 \text{ V}$ (vs. Li), a very smooth, single slope discharge curve typical of amorphous materials is seen in all discharge curves. The extent of this region is very similar at all rates with the exception of the highest one ($C/0.28$). About one equivalent of lithium per mole of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ is inserted in the high voltage region.

The intermediate voltage region extends from 2.7 to 2.4 V (vs. Li) is characterized by the presence of a voltage plateau in the discharge curves. The extent of the plateau sharply decreases with the discharge rate. It almost disappears at the highest discharge rate ($C/0.28$). Finally, the low voltage region extends to voltages lower than 2.4 V (vs. Li). In this final region, the discharge rate appears to strongly affect the voltage slope and the delivered capacity. Once more, the extent of the third voltage region ($V < 2.4 \text{ V}$) at the highest discharge rate ($C/0.28$), is very limited. Interestingly, the low-rate discharge curves ($C/22$, $C/10$ and $C/4.3$) show the onset of a second plateau. Because of the low voltage (1.5 V), the plateau does not have any practical interest for a cathode material and no further investigation has been carried out for the purpose of the present work. Nevertheless, further research work is in progress to investigate the low-voltage behavior of the copper-doped material.

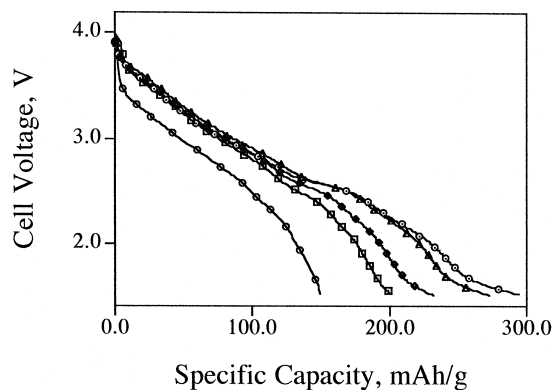


Fig. 2. Voltage vs. specific capacity curves as obtained by discharging a spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in a coin cell assembly at different rates. Discharge current densities and discharge times: 0.041 mA/cm^2 and 22 h (dotted circles), 0.083 mA/cm^2 and 10 h (triangles), 0.166 mA/cm^2 and 4.3 h (diamonds), 0.413 mA/cm^2 and 1.5 h (squares), 1.654 mA/cm^2 and 0.28 h (circles). Active material loading: 3 mg/cm^2 .

Summarizing, the spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ showed excellent rate performance by delivering a capacity as high as 150 mA h/g per gram in a 17 min (at 1.654 mA/cm²) discharge and 295 mA h/g at the lowest current density used (22 h discharge time at 0.041 mA/cm²). The rate performance of spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrodes in terms of specific energy and power are illustrated in Fig. 3 as a function of the current density and the specific current. The data were computed from the discharge curves showed in Fig. 2. The cell was able to deliver specific energies from 400 to 760 mW h/g with discharge rates from C/0.28 to C/22. Fig. 3 also shows that the specific power delivered by the spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrodes scaled linearly with the current density from 35 mW/g at 0.041 mA/cm² to 1.44 W/g at 1.654 mA/cm².

High-rate, pulsed discharge tests were performed on a spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in coin cell assembly. Fig. 4 illustrates the cell voltage behavior during the test. For comparison, the voltage behavior of the same cell under a complete, low-current insertion/release cycle is also reported (dashed line; current density: 0.112 mA/cm²). The high-rate, pulsed discharge test was carried out by first discharging one-third of the cell capacity with a very high current density (solid line; current density: 2.25 mA/cm²). The cell was then tested by pulsed discharge. The latter consisted in the application of a high current density pulse for 1 s and in the relaxation period of 19 s. A complete pulse cycle lasted for 20 s and involved the same amount charge than in the low-current discharge over the same time period, i.e., the same overall discharge rate. The cell voltage behavior during the pulsed discharge is indicated in the figure by the small points. The cell voltage behavior during the high-rate/pulsed discharge is excellent. In the initial high-rate insertion step (solid line), the cell showed a voltage decrease steeper than in the low-rate discharge (dashed curve) but when the overall

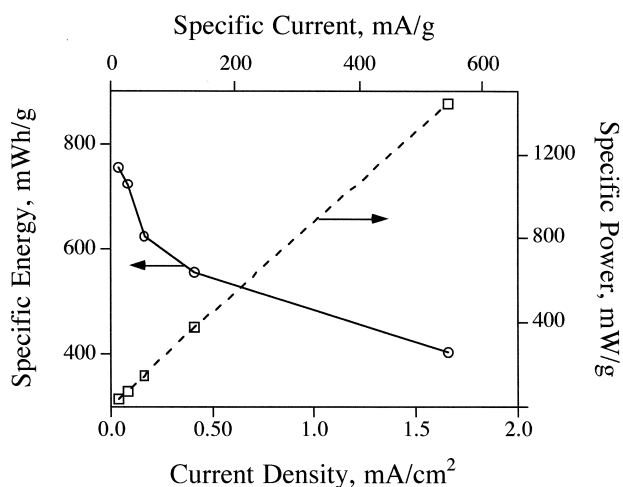


Fig. 3. Specific capacity and specific energy vs. current density and specific current of a spray coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in a coin cell assembly for different discharge rates.

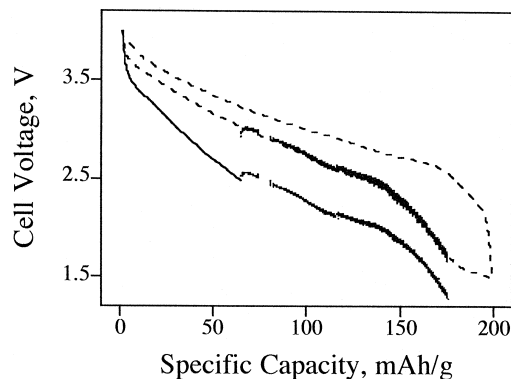


Fig. 4. Cell voltage behavior vs. specific capacity of a spray coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in a coin cell assembly upon a high rate (dashed) and pulsed discharge (dots). Current density: 2.25 mA/cm². Specific current: 545 mA/g. Active material loading: 4.1 mg/cm². See text for a description of the test procedure. The solid line illustrates the voltage behavior of the same cell upon low current charge/discharge cycle. Current density: 0.112 mA/cm². Specific current: 27 mA/g. Active material loading: 4.1 mg/cm².

rate was reduced (pulsed discharge), the cell voltage immediately matched the low-rate discharge curve (when no current was applied). During the high-rate pulses, the cell voltage dropped a few hundred millivolts but it always matched the low-rate cell voltage curve during the relaxation period. Such a fast relaxation is a clear indication of the absence of major diffusion limitations within the solid phase of the spray-coated cathode. The cell polarization was mostly due to the electrolyte ohmic drop and/or the charge of the electrolyte–electrode double layers. Although of the stressing discharge condition, the cell was able to deliver 88% of the low-rate capacity in 3.2 h discharge.

A second high-rate, pulsed discharge on a low-current background discharge test was also performed. The results are shown in Fig. 5 in which is also reported the standard, low-current insertion/release cycle (dashed line; current density: 0.112 mA/cm²). The high-rate, pulsed discharge on a low-current background test consisted in the application of a high current density (2.25 mA/cm²) pulse for 5 s alternated with a low current density (0.112 mA/cm²) background discharge period of 95 s. A complete pulse cycle lasted for 100 s with a similar amount of charge involved in each period (50% duty cycle). The cell behavior during the test is excellent. The cell voltage (solid line) during the background discharge periods always matched the voltage of the cell discharged at low current density (dashed line). To further stress the test, the pulse schedule was changed when 40% of the cell capacity was already delivered. The high-current pulse period was increased to 20 s, i.e., 80% duty cycle. Once more, the cell voltage during the background discharge periods was able to match the voltage of the cell discharged at low current density. After delivering of about 140 mA h/g capacity, the cell

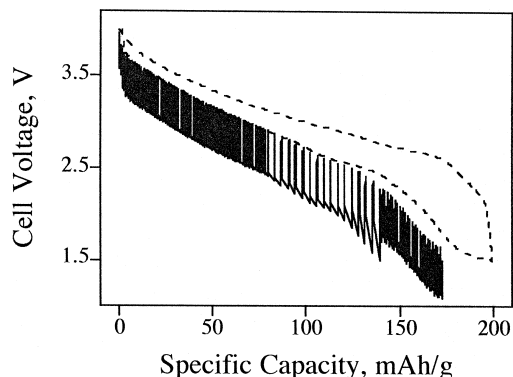


Fig. 5. Cell voltage behavior vs. specific capacity of a spray coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in a coin cell assembly upon a high-rate pulsed discharge over a low-rate background current (solid line). Pulse current density: 2.25 mA/cm^2 . Pulse specific current: 545 mA/g . Background current density: 0.112 mA/cm^2 . Background specific current: 27 mA/g . Active material loading: 4.1 mg/cm^2 . See text for a description of the test procedure. The solid line illustrates the voltage behavior of the same cell upon low current charge/discharge cycle. Current density: 0.112 mA/cm^2 . Specific current: 27 mA/g . Active material loading: 4.1 mg/cm^2 .

voltage behavior indicated a substantial electrode polarization and the 50% duty cycle test was resumed. Despite of the heavy discharge conditions, the cell was able to deliver more than 80% of its low-rate capacity in 1.75 h.

The excellent performance showed by the coin cell under high-rate/pulsed discharge tests confirms the capability of the spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrodes to deliver high capacity together with high rate performance.

The characterization of the spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode performance in coin cell assembly, was extended to long-term cycle tests. The results are illustrated in Fig. 6 where is reported the cell delivered capacity upon repetitive galvanostatic charge and discharge cycles. The spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode was able to deliver about 170 mA h/g in 80 min discharge at a current density of 0.2 mA/cm^2 over more than 450 cycles. The excellent cycle performance of copper-doped vanadium oxides has been

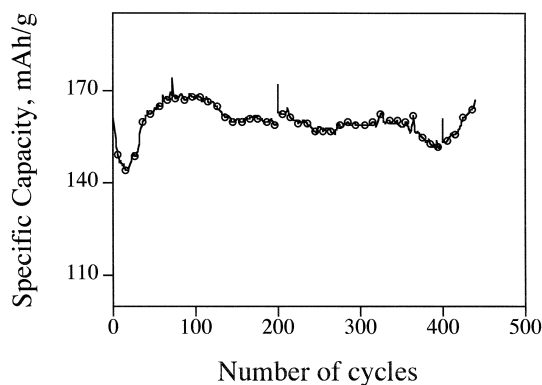


Fig. 6. Specific capacity vs. number of cycles of a spray coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ electrode in a coin cell assembly. Current density: 0.15 mA/cm^2 . Specific current: 136 mA/g . Active material loading: 1.1 mg/cm^2 .

shown to be a peculiar characteristic of the materials among the gel based V_2O_5 materials [10].

Investigation of the feasibility of a battery with the lithium-ion chemistry based on spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel was also carried out. The anode was prepared by casting a mixture of MCMB, Super P (MMM carbon) and Kynar (ELF-Atochem) in cyclopentanone. Prior assembling the coin cell, the anode was loaded with lithium by simply short circuiting the carbon anode and a piece of lithium in the electrolyte. The electrolyte used for the carbon pre-lithiation and in the $\text{Cu}_{0.1}\text{V}_2\text{O}_5/\text{MCMB}$ coin cell was a 1 M solution of LiClO_4 in EC-DMC (2:1). The $\text{Cu}_{0.1}\text{V}_2\text{O}_5/\text{MCMB}$ cell was designed to be cathode limited. The performance of such a cell upon repetitive charge/discharge cycling at a current density of 0.173 mA/cm^2 is illustrated in Fig. 7. The cell was initially cycled between 1.5 and 4.0 V voltage cut-offs. The first cycle capacity was about 170 mA h/g , i.e., almost as much as in lithium-metal anode configuration. Unfortunately, the lithium-ion cell did not show the same behavior of the lithium-metal one in terms of cycle performance. After 70 cycles the delivered capacity decreased to 40% of the initial one. More than 75% of the initial capacity was recovered by using the 4.1 V anodic cut-off but a somewhat high capacity fading was still observed. After 160 cycles the delivered capacity was about 60% of the initial one. The reason of the capacity fading was found in the slight solubility of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ into the electrolyte used in the lithium-ion cell. It has been found that the problem is characteristic of DME containing electrolyte. No dissolution of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ has been detected in lithium-metal-based coin cell that use propylene carbonate as liquid component of the electrolyte. Further work is needed to individuate an electrolyte that would optimize the performance of the lithium-ion cell based on copper-doped vanadium oxide cathode. Nevertheless, the results shown in Fig. 7 clearly confirm the feasibility of such a system.

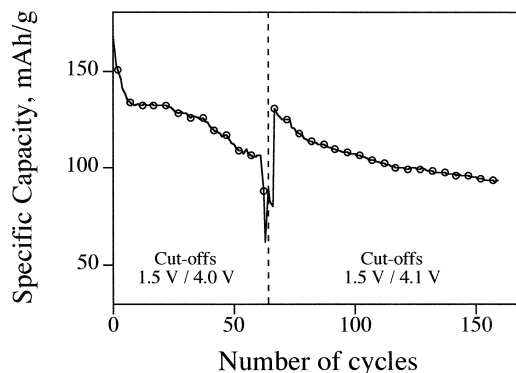


Fig. 7. Specific capacity vs. number of cycles of a lithium-ion coin cell containing a spray coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ cathode and a MCMB carbon anode. The electrolyte was in 1 M LiClO_4 in EC-DME (2:1). Current density: 0.17 mA/cm^2 . Specific current: 133 mA/g . Active material loading: 1.3 mg/cm^2 .

4. Conclusions

Spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel cathodes have shown excellent performance in coin cell assembly. The full lithium insertion capacity of the material (300 mA h/g) is achieved in 22 h discharges. Such a high capacity corresponds to a specific energy as high as 750 mW h/g.

The rate performance was also excellent. The cells were able to deliver above 150 mA h/g capacity, corresponding to a specific energy of about 400 mW h/g, in very fast discharges (ca. 17 min). The specific power in this test exceeded 1400 mW h/g. Spray-coated $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel cathodes were able to deliver about the intercalation capacity and a higher energy than the latest developed amorphous manganese oxyiodide [14] using higher current density. In addition, the cathodes showed very good cycle performance with a full capacity retention over 450 cycles.

Finally, the feasibility of lithium-ion batteries based on the copper-doped vanadium oxide cathode has been demonstrated.

Acknowledgements

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