

The Organic-Inorganic Polyaniline/V₂O₅ System

Application as a High-Capacity Hybrid Cathode for Rechargeable Lithium Batteries

M. Lira-Cantú and P. Gómez-Romero*^z

Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, E-08193 Bellaterra, Barcelona, Spain

The application of a hybrid polyaniline/V₂O₅ cathode material in reversible lithium electrochemical cells is reported. We have studied the influence of synthesis conditions and subsequent treatments of this hybrid electrode under oxygen in order to optimize its performance as a lithium-insertion cathode. The temperature and duration of this treatment are key parameters in determining the final specific charge of the cathode. The optimal material yielded a specific charge as high as 302 Ah/kg measured at a low discharge rate (C/48) corresponding to the insertion of 2.72 lithium ions per formula unit (C₆H₄N)_{0.6}V₂O₅·0.3H₂O. Higher scan rates of C/12 lead to specific capacities of 200 Ah/kg. The thermal and electrochemical stability of the hybrid electrode, especially in relation to the decomposition of the organic polymer and its effect on battery performance and cyclability, are also discussed. © 1999 The Electrochemical Society. S0013-4651(98)08-027-6. All rights reserved.

Transition-metal oxides are the most common candidates for cathodes in the development of lithium and lithium-ion battery technologies. Thus, in the latter, the oxide LiCoO₂ is used in rechargeable lithium batteries from Sony,¹ whereas LiMn₂O₄ represents its major contender in secondary lithium batteries.² These materials address the need for high-voltage cathodes (positive electrodes) required for lithium-ion batteries but can only cycle half a lithium ion per metal atom. Other crystalline oxides such as V₂O₅ or MnO₂ have also been used as cathodes in rechargeable lithium batteries.^{3,4} They present lower voltages but are also limited in the amount of charge that can pass reversibly during cycling. Certain amorphous derivatives of these oxides appear to avoid this problem but have a limited cyclability.^{5,6} Thus, V₂O₅ xerogels can accumulate reversibly up to 0.9 Li⁺ ions per V atom, substantially more than the 0.5 Li per V that the parent crystalline V₂O₅ oxide. The cyclability of the gel is also somewhat improved but still falls steadily with the number of cycles.⁷⁻¹³

Conducting organic polymers (COPs) constitute a different category of materials which were recognized as potential insertion electrodes after showing a suitable reversible redox chemistry. In this case the conductivity and plastic nature of these materials are among the most important factors in favor of their application, and light plastic batteries were envisioned. COPs have nevertheless suffered from other drawbacks such as high self-discharge rates and an inconvenient insertion-deinsertion mechanism involving anions.¹⁴⁻¹⁶ Attempts at solving this latter problem have included the synthesis of COPs with large or even polymeric organic anions as doping species in order to fix them in the structure.¹⁷⁻¹⁹ Examples of this approach include derivatives of COPs with propane sulfonic acid,²⁰ *o*-aminobenzenesulfonic acid,^{21,22} camphorsulfonic acid,²³ and also self-doped derivatives.²⁰⁻²² In all these cases, however, the counterions are electrochemically inactive.

We have recently undertaken a study of organic-inorganic hybrid materials based on COPs and electroactive inorganic species as insertion electrodes for rechargeable lithium batteries.²⁴⁻³¹ These hybrids are formed by COPs such as polyaniline (PAni), polypyrrole (Ppy), or polythiophene (PT), and redox-active inorganic clusters such as [PMo₁₂O₄₀]³⁻,²⁴⁻³⁰ molecules such as [Fe(CN)₆]⁻,³¹⁻³³ or oxides including MnO₂,⁴ LiMn₂O₄, or V₂O₅.^{28,34-36} The intercalation of aniline into V₂O₅ and the corresponding polymerization were the subject of earlier studies,³⁷⁻⁴⁸ whereas the use of polyaniline-intercalated V₂O₅ in lithium cells has also been recently reported.^{34,35,45,48} Until now the synthesis of the hybrid material has been carried out with preformed films of V₂O₅ oxide.^{34,40,45,49} In a previous paper we have reported a modified synthetic procedure based on the "in situ" polymerization of aniline by direct reaction with V₂O₅

hydrogels and the optimization of that synthesis. We also established the existence of two distinct phases in the PAni/V₂O₅ system. Here we report the application of an optimized material as a lithium-insertion cathode, either as prepared or after mild thermal treatments under oxygen atmosphere. We analyze the thermal and electrochemical stability of these hybrid materials and finally their performance in lithium reversible cells, including preliminary cycling behavior.

Experimental

Reagents.—KBr Fourier transform infrared (FTIR) grade 99+ % and aniline 99.5% were purchased from Aldrich, H₃PO₄ 85% and H₂SO₄ 96% from Panreac, and (NH₄)₂Fe(SO₄)₂·6H₂O 99.9% from Carlo Erba. NaVO₃ 99.5% and the ion-exchange resin DOWEX 50×2-100 were purchased from Sigma. Aniline was distilled under vacuum before use; all other reagents were used as received. Ethylene carbonate (EC) and anhydrous dimethoxyethane (DME) were purchased from Aldrich. EC:DME electrolyte solvents were handled under argon. A battery electrolyte mixture was made by mixing EC (ethylene carbonate, no further purification) and anhydrous DME (dimethoxy ethane) in a 1:1 ratio. LiClO₄ electrolyte salt was dried at 155°C under dynamic vacuum for 12 h. Once made, battery electrolyte solutions were purged with argon before use.

Measurements.—A Carlo Erba CHN EA 1108 system was used for elemental analyses. Vanadium(V) in the gel was analyzed by a potentiometric titration method described elsewhere⁵⁰ with a CRI-SON potentiometer. The vanadium content in the final hybrid material was analyzed after complete calcination of the organic part by atomic absorption spectroscopy in a Perkin Elmer 2100 apparatus. The resistivities of pelletized samples were measured by the van der Pauw technique⁵¹ with a Hewlett Packard 2432 multimeter. Samples of the materials were dried under dynamic vacuum until a constant weight was reached and pressed into pellets onto which four copper leads were attached with silver paint. Infrared spectra were recorded as KBr pellets with a Nicolet 710 FTIR spectrophotometer. Thermal treatments under oxygen were performed in a Perkin Elmer TGA7 thermogravimetric balance with a heating rate of 1°C/min. Powder X-ray diffraction analyses were performed in a Rigaku Ru-200B apparatus from 3 to 60° with Cu K α radiation. Electrochemical studies were carried out with a computer-controlled EG&G Princeton Applied Research 270A potentiostat/galvanostat in a three-electrode cell with an Ag/AgCl reference electrode and a Pt counter electrode for characterization in aqueous media, whereas Li metal as reference and counter electrode was used for characterization in organic media. As electrolytes we used HClO₄ and LiClO₄ 1 M for aqueous and organic media, respectively. Compact reversible electrochemical cells were set up in Swagelok test cells² using a Labconco 50700 glove box that allows for water and oxygen removal to less than 1 ppm. Li foil (16-13 mm diam and 0.1 mm thick) was used as the

* Electrochemical Society Active Member.

^z E-mail: pedro.gomez@icmab.es

negative electrode, an intimate mixture of the hybrid material and carbon Super P (20%) as the positive electrode, and a solution of LiClO_4 1 M in a 1:1 mixture of EC/DME was used as electrolyte. The cells were tested with charge/discharge cycles at constant current performed with an ARBIN model BT2042 potentiostat.

Synthesis of the hybrid $(\text{C}_6\text{H}_4\text{N})_{0.6}\text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$.—Vanadium pentoxide gels were prepared by an ion-exchange method reported elsewhere.^{52,53} Vanadium(V) is responsible for aniline polymerization; thus, before synthesis of the PANi/ V_2O_5 hybrid, a potentiometric titration of the V_2O_5 gel with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was carried out⁵⁰ in order to determine the exact amount of V(V) present in the gel. The hybrid PANi/ $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ material was prepared by slow and direct addition of an aniline solution over the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gel. Thus, 50 mL of an aniline solution (1.8 mL in water) were added dropwise to 43 mL of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gel [0.16 M in V(V) gel previously aged during 1 month]. The reaction mixture was kept at 0°C with rapid and constant stirring for 120 h. The fine powder obtained was washed with water until the yellow color of the filtrate disappeared.

Results and Discussion

Synthesis and basic characterization of the hybrid $(\text{C}_6\text{H}_4\text{N})_{0.6} \cdot x\text{H}_2\text{O}$.—The synthesis of PANi/ V_2O_5 takes place with the oxidative polymerization of aniline at the expense of V_2O_5 reduction which could subsequently reoxidize in air.³⁶ The polymerization process has been reported to continue for long times after the initial intercalation of aniline monomers into the oxide. In principle we considered a -0.2 negative charges per V in V_2O_5 gels⁵² and a $+0.5$ positive charge per ring for PANi in its conductive emeraldine salt form.⁵⁵ Thus, a ratio of 0.8 aniline rings per V_2O_5 could be expected. Notwithstanding, we tried the reaction with different nominal aniline/ V_2O_5 ratios and found that it is possible to obtain hybrid adducts with different stoichiometries^{29,56} and thus different properties for the final hybrid materials. For our main product, prepared as described in the Experimental section, we used a 3:1 aniline: V_2O_5 ratio. This product (vacuum dried at room temperature) showed the following chemical analyses: experimental: 17.87% C, 1.15% H, 3.48% N, 41.72% V; calculated for $(\text{C}_6\text{H}_4\text{N})_{0.6} \cdot \text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$: 17.916% C, 1.253% H, 3.482% N, 42.21% V.

Electrical conductivity values as high as 0.09 S/cm were achieved by our hybrid materials and maintained their original values after 15 days. We have reported these relatively high values in comparison with other related materials.^{36,41} Optimization of the conductivities of the hybrids is obviously not intended as a way of optimizing their electrochemical properties but rather as a way of obtaining the polymer in the proper conducting form.

The FTIR spectrum of this PANi/ V_2O_5 hybrid (see Fig. 1a) presents a series of bands in the low-frequency region which have been previously assigned to V_2O_5 ⁴⁰ bands at 512, 760 cm^{-1} for the V—O—V stretching modes and at 1038 cm^{-1} for the V=O stretching. Bands corresponding to the organic part appear in the 1000–2000 cm^{-1} range and are typical of polyaniline in its emeraldine form.⁵⁷

In principle both the organic polyaniline and the inorganic V_2O_5 gel are essentially amorphous polymers, although V_2O_5 xerogels present in fact some crystallinity, especially when obtained in the form of films (with preferential orientation).⁵³ Powder X-ray diffraction patterns of our hybrid materials present very broad peaks derived from the V_2O_5 network overlapped with diffuse scattering features associated to the presence of polyaniline. Overall, the crystallinity of the hybrids is substantially lower than that of a V_2O_5 xerogel prepared from the same parent V_2O_5 hydrogel. Figure 2 shows the powder X-ray diffraction pattern of the optimized hybrid PANi/ V_2O_5 before oxygen treatment. The strong peak at low angles corresponds to the 001 from the V_2O_5 structure. In the hybrid it appears at $2\theta = 6.25^\circ$ ($c = 14.14 \text{ \AA}$), whereas in the corresponding V_2O_5 xerogel this peak showed up at 7.78° ($c = 11.36 \text{ \AA}$). This expansion of 2.78 \AA is in good agreement with the results reported earlier^{34,36,38,40,41,44,49} and corresponds to the replacement of water between the V_2O_5 layers (2.8 \AA) and the insertion of one monolayer of polyaniline. Thus, the net dimension associated to the insertion of

PAni is approximately 5.58 \AA , which according to previous reports would imply an orientation of polyaniline chains with the rings approximately perpendicular to the V_2O_5 slabs.^{40,49}

Treatment under oxygen.—Earlier results by Nazar et al.^{34,35,45,48} showed the benefits of O_2 treatments on the specific charge of the hybrid PANi/ V_2O_5 used as a cathode in lithium cells. The reason why oxidative thermal treatment improves the electrochemical performance of the hybrid is to be found in the chemical modification suffered by their components. During synthesis of the PANi/ V_2O_5 hybrid material, V(V) is reduced to V(IV) and aniline is oxidized to polyaniline; thus, V(IV) is present in the hybrid material after synthesis. Oxygen treatments help V(IV) to be reoxidized to V(V). A higher oxidation state of V results in higher initial cell voltage and higher specific capacity. Based on these results, we have analyzed the influence of time and temperature of a mild thermal treatment under oxygen of the materials obtained. We have carried out treatments at 80, 110, and 145°C for 5, 15, and 24 h, respectively.

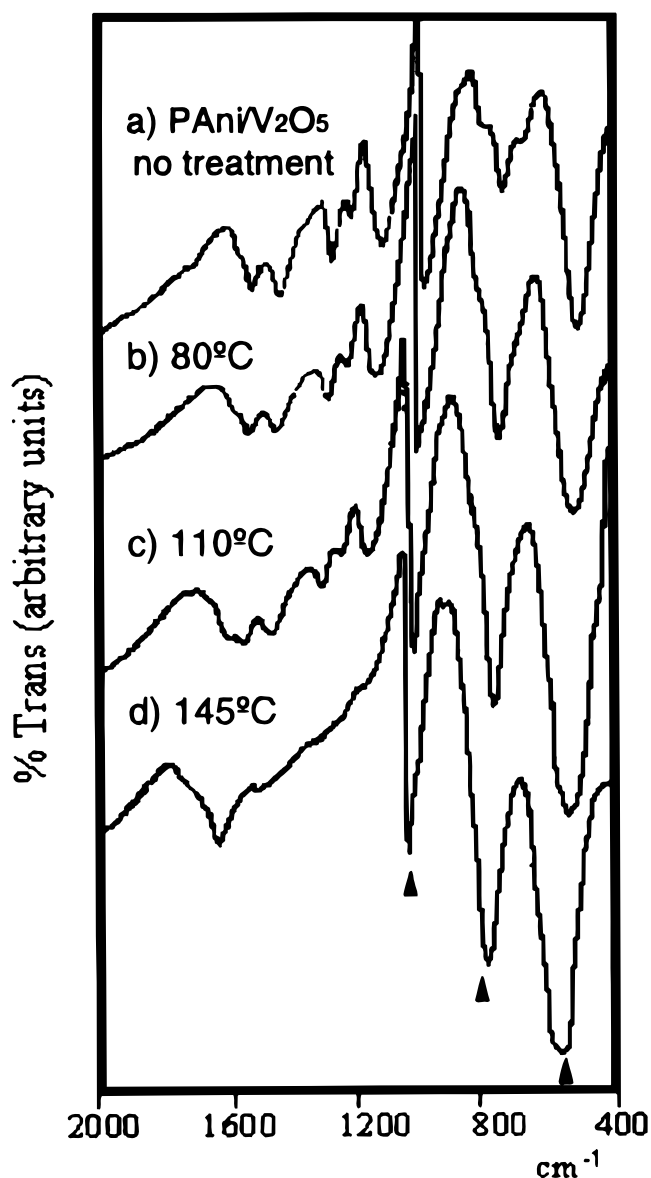


Figure 1. FTIR spectra for the hybrid PANi/ V_2O_5 ($\text{C}_6\text{H}_4\text{N})_{0.6}\text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$ treated in O_2 atmosphere: (a) as prepared, (b) 80°C/15 h, (c) 110°C/15 h, and (d) 145°C/15 h. Triangles mark the peaks assigned to V_2O_5 vibrational modes (see text).

We must be aware of a possible degradation of the organic part of the hybrids PAni/V₂O₅ as the temperature increases. To check for that we carried out FTIR analyses of materials treated at different temperatures. Figure 2 shows the FTIR spectra of the sample (a) before treatment and after treatments of 15 h at (b) 80, (c), 110, and (d) 145°C. These spectra show the degradation of the hybrid at the higher temperatures. In particular, the bands assigned to the organic polymer suffer increasingly important changes at temperatures above 110°C. This degradation corresponds to the organic part of the hybrid, because only bands between 1000 and 2500 cm⁻¹ are affected. We could not include all the spectra recorded in this study, but we could detect increasing degradation as treatment times were increased for each temperature. Slow degradation processes taking place during heating treatments were thus detected in all experiments, except for the sample treated at 80°C (the lowest temperature), which showed no signs of degradation even after 24 h treatments.

Studies as cathode for lithium batteries.—Water in V₂O₅ xerogels plays an important detrimental role in their performance as cathodes for rechargeable lithium batteries. West et al.⁹ showed the relationship between thermal treatments of V₂O₅ xerogels related in turn to their water contents and their final performance. Thus, they showed how V₂O₅ xerogels treated at 300°C (which eliminates coordinated water) were able to intercalate larger amounts of lithium ions than the corresponding gels treated at 100°C (which removes only weakly bound water).⁹

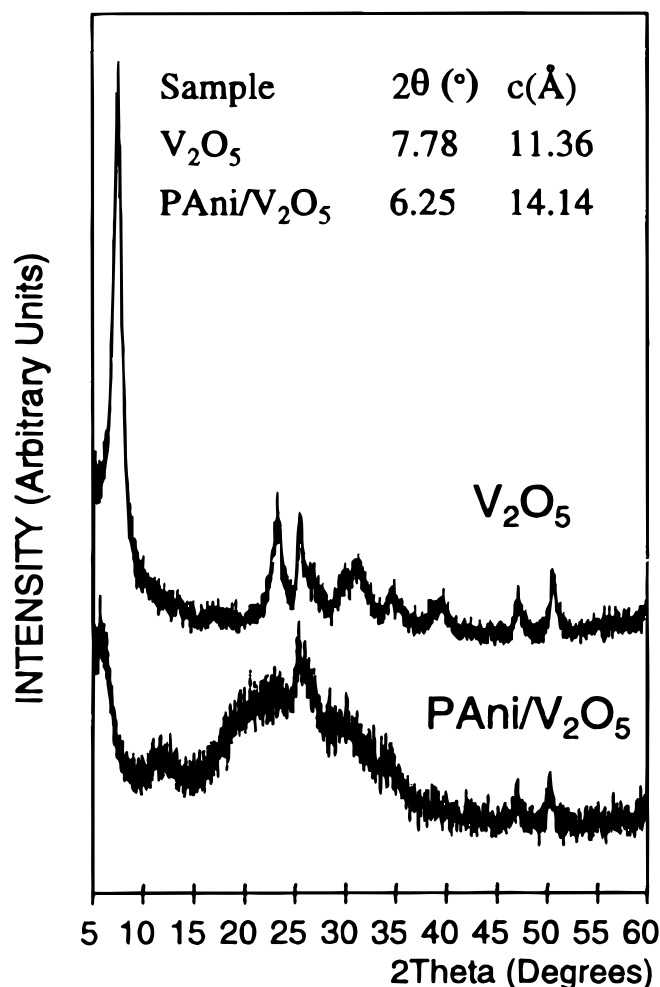


Figure 2. Powder X-ray diffraction patterns of the optimized hybrid (C₆H₄N)_{0.6}V₂O₅·0.3H₂O and for the V₂O₅ xerogel. The broad features at 12 and 25° are associated to the growth of the PAni network.

Polyaniline intercalation into V₂O₅ not only represents the pillar of oxide slabs with electroactive conducting chains, it also contributes to the elimination of strongly bound coordinated water from the gel. Figure 3 shows the influence of thermal treatments on the lithium intercalation capacity of our V₂O₅ xerogel and the hybrid prepared from the same hydrogel. All the cycles shown were recorded at low current, approaching near-equilibrium conditions (C/48 rate). The hybrid as-prepared PAni/V₂O₅ presents a specific charge comparable to that of the V₂O₅ xerogel treated at 250°C, even though that sample of hybrid had not been subject to any thermal treatment. The specific charge of 161 Ah/kg for as-prepared PAni/V₂O₅ (Fig. 3a) is higher than that measured for the V₂O₅·H₂O xerogel, dried at 100°C (124 Ah/kg) and is close to that of the V₂O₅ xerogel dried at 250°C (183 Ah/kg). After a mild thermal treatment of 5 h at 80°C under O₂, the PAni/V₂O₅ hybrid materials produced a substantially improved result with a specific charge of 302 Ah/kg (Fig. 3b), corresponding to 2.72 electrons per formula unit [(C₆H₄N)_{0.6}V₂O₅·0.3H₂O].

These results have several implications. First, they show the great importance of mild thermal treatment under oxygen in optimizing the specific charge of our hybrid materials. Second, we can conclude that our hybrid material shows a specific capacity much higher than that of the corresponding V₂O₅ xerogel treated at the same temperature. Polyaniline must play a central role in the improved specific charge as it is itself an electrochemically active component (see the following discussion).

We have also screened different conditions for the thermal treatment of the hybrids in order to determine the effect in their initial capacity. We treated the samples under oxygen, during different periods of time (5, 15, and 24 h), and at different temperatures (80, 110, and 145°C). The results obtained are summarized in Fig. 4 by plotting the specific charge obtained for the first discharge of each hybrid material as a function of their treatment time. In all cases we used a slow discharge rate (C/48) to analyze the materials under close-to-equilibrium conditions. Figure 4 shows a drastic change in the specific charge of the different samples. Higher values are obtained for sample treated at 80°C for short periods of time, with a treatment of 5 h leading to the highest values of 302 Ah/kg.

In order to determine why these treatments so drastically affect the capacity of the hybrid materials, we have analyzed plots of incremental capacity (*dQ/dV*) for the discharge curves of each of the differently treated materials. Figure 5 shows incremental capacity plots calculated from the first discharge curve of each sample. Included are the as-prepared hybrids PAni/V₂O₅ without treatment (Fig. 5a) and hybrids after different treatments (Fig. 5b-d), as well as the V₂O₅ xerogel alone for comparison (Fig. 5e).

Let us first compare the incremental capacity curve of the hybrid as prepared (Fig. 5a) with that of V₂O₅ (Fig. 5e). The former presents a sharp peak at 2.55 V with a shoulder at about 2.3 V (Fig. 5a),

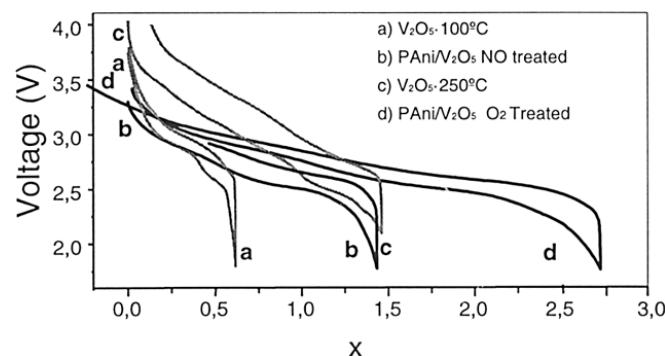


Figure 3. First discharge (C/48) obtained for (a) V₂O₅ xerogel dried at 100°C, (b) hybrid PAni/V₂O₅ as prepared, without treatment, (c) V₂O₅ xerogel dried at 250°C, and (d) hybrid PAni/V₂O₅ treated at 80°C for 5 h. The indicated values of *x* were calculated for the formula Li_{*x*}(C₆H₄N)_{0.6}V₂O₅·0.3H₂O for curves (b) and (d) and for Li_{*x*}V₂O₅·*y*H₂O for curve (a) (*y* = 1) and for curve (c) (*y* = 0.5).

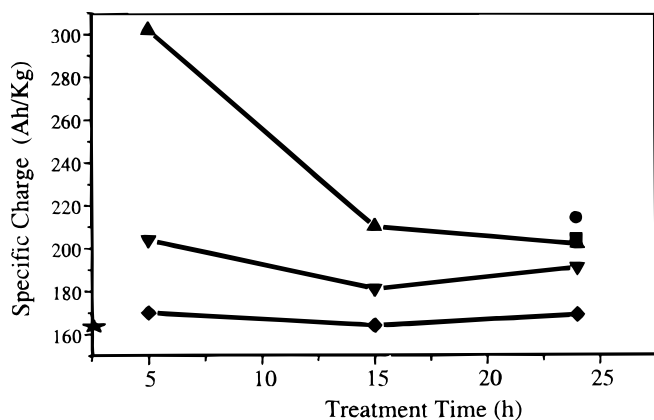


Figure 4. Specific charge vs. oxygen treatment for the hybrid PAni/V₂O₅ during the first discharge at C/48. Treatments at (●) 30, (■) 50, (▲) 80, (▼) 110, and (◆) 145°C, (★) hybrid without treatment.

which is absent in the case of the V₂O₅ xerogel and can therefore be assigned to the electrochemical activity of polyaniline in the hybrids. A broader peak at 2.9 V is common to all samples; it is present for all the hybrids and also for V₂O₅ at the same voltage and should be assigned to the inorganic polymer. In fact, the incremental capacity curve of V₂O₅ xerogel presents also a second broad peak at 2.6 V which in the hybrids is obscured by the sharp feature associated to PAni activity.

A second important conclusion can be reached from the incremental capacity curves in Fig. 5 and their evolution with the temperature and length of thermal treatments. Comparing the series in Fig. 5b, c, and d we can see the collapse of the sharp PAni peak at 2.55 V as temperature increases.

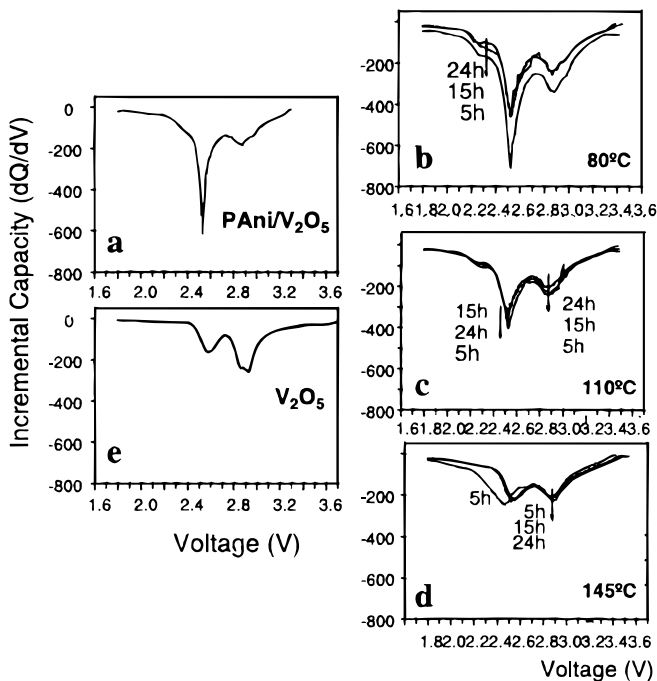


Figure 5. Incremental capacity curves (dQ/dV) calculated from the corresponding first discharge curves of a series of PAni/V₂O₅ samples subject to different thermal treatments: (a) hybrid PAni/V₂O₅ after synthesis, (b) (c), and (d) hybrid PAni/V₂O₅ with oxygen treatment as indicated, and (e) V₂O₅·H₂O xerogel.

PAni but not that of V₂O₅ appears to decrease in going from treatments at 80-110°C and finally to 145°C. After treatments at that temperature the electroactivity of the hybrid appears to be reduced to just that of V₂O₅. Although these temperatures are too low for the complete decomposition of PAni, we must assign this decrease in activity to a degradation of polyaniline affecting its redox chemistry and electrochemical activity, a degradation which was also apparent from changes in the IR spectra of samples of hybrids treated at mildly high temperatures (see Fig. 2).

Comparison of incremental capacity plots for samples with and without PAni electroactivity allow for an approximate estimate of the contribution of PAni and V₂O₅ to the total capacity. For this purpose we have used curves for samples treated for 15 h at 80°C and for 24 h at 145°C (chosen due to the comparable magnitudes of the peak at 2.9 V in each) (Fig. 5). From the difference of specific charge of both curves we estimate the contribution of PAni to be ca. 20% of the total capacity for samples with full PAni activity (i.e., those treated at 80°C). This leads to a contribution per formula unit for 60 Ah/kg (0.55 e⁻) for PAni and 242 Ah/kg (2.18e⁻) for V₂O₅, considering that there are 0.6 aniline rings per formula unit, this results in 0.9e⁻ per ring in the case of PAni and 2.18 e⁻ per V₂O₅ in the hybrid. These values are larger than for samples of the gel alone treated under comparable conditions as the hybrid, which indicates a synergic behavior between PAni and V₂O₅ in the hybrid materials.

On the other hand, the characteristics of these hybrid materials are very much dependent on the particular synthetic conditions. When synthesis is carried out under the exact conditions described in the Experimental section, we have found the materials can be prepared reproducibly.

We must note that our results differ somewhat from previous reports on the performance of PAni/V₂O₅ materials as lithium-insertion cathodes. Nazari et al. have reported values of 165 Ah/kg (at constant current or 370 Ah/kg at galvanostatic intermittent lithiation at ~C/12) for these materials after treatments at 150°C/8 h under oxygen, but we have found those temperatures to be too high for our materials and have attained higher specific charges for samples treated at lower temperatures.

Finally, we mention preliminary results concerning the cyclability behavior of the PAni/V₂O₅ hybrids. This is an aspect which has not been addressed in previous articles by other groups, but it is of considerable importance. Figure 6 shows the variation of specific charge of the materials with the number of cycles. This results are probably better than those previously obtained for V₂O₅ xerogels with a similar thermal history and water content as our hybrids.^{5,7,9-12,58} Yet our data show a slow but continued decrease in specific charge and point out the need for an improved cyclability of these materials.

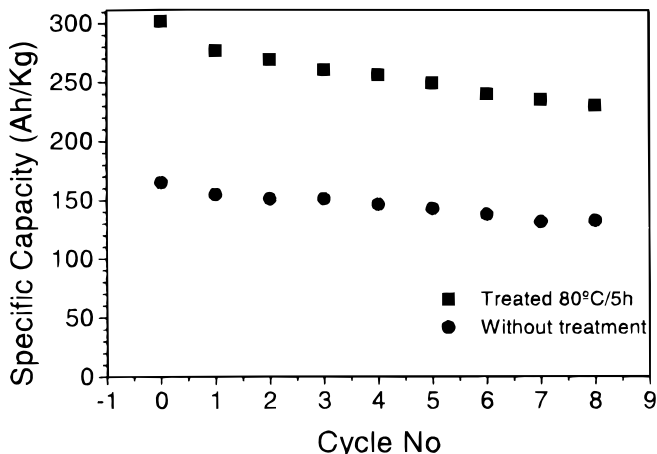


Figure 6. Variation of the specific charge of PAni/V₂O₅ hybrids with the number of cycles. Data shown are for the material as prepared and after treatment at 80°C (C/48 rate).

Conclusions

We have used the hybrid PANi/V₂O₅ of formula (C₆H₄N)_{0.6}V₂O₅·0.3H₂O as the active cathode material in reversible lithium cells. An optimized procedure for the synthesis of this hybrid leads to a material with a specific charge as prepared of 161 Ah/kg at low discharge rate (C/48). Further thermal treatments of the hybrid under oxygen can substantially improve this result. A mild treatment at 80°C for 5 h results in an improved specific charge of 302 Ah/kg at the same discharge rate, which corresponds to the insertion of 2.72 lithium ions per formula unit (C₆H₄N)_{0.6}V₂O₅·0.3H₂O. With an average voltage of 2.7 V, this leads to an energy density of 815 Wh/kg. Under higher discharge rates of C/12, the corresponding value of specific charge is 200 Ah/kg (540 Wh/kg energy density). Heating at high temperatures leads to a poorer performance associated with the suppression of the electrochemical activity of PANi in the hybrid material.

Acknowledgments

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