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Flexible cathode materials based on V_2O_5 xerogels reinforced with electroactive $Ba_6Mn_{24}O_{48}$ whiskers

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Flexible cathode materials based on V_2O_5 xerogels reinforced with a new type of whiskers containing structural tunnels available for proton intercalation are prepared and their performance is tested in alkaline electrochemical cells.

The design of new batteries with improved performance demands the search for new cathode materials serving as an effective matrix for intercalation. V_2O_5 xerogels with a layered structure available for ion intercalation are promising materials for positive electrodes.[1,2] However, V_2O_5 xerogels are brittle and it would be important to improve their mechanical strength without a drastic loss in electrochemical performance. This could be achieved by reinforcing the xerogel with electrochemically active fibers enhancing fracture toughness and the flexural strength of the material. Carbon, silicon carbide and silicon nitride whiskers are widely used as reinforcing fibers.[3,4] In electrochemical cells, cellulose fibers are effective to strengthen the polymer electrolyte material.[5] In this work, we propose a new preparation technique of V_2O_5-based flexible electrodes reinforced with new electroactive $Ba_6Mn_{24}O_{48}$ whiskers.[6,7]

To prepare V_2O_5 gels by VO_3^- polycondensation, a V_2O_5 suspension was made by passing a 0.25 M sodium vanadate solution through a cation-exchange column (Amberlite IR112). The yellow solution coming out of the column was sonicated in a standard ultrasonic bath (Saphire, Russia). The viscosity of the solution significantly increased due to the $V_2O_5{\cdot}nH_2O$ condensation leading to the formation of a V_2O_5 gel accompanied by a colour change to dark red.[11]

The reinforcing $Ba_6Mn_{24}O_{48}$ whiskers were grown according to the chloride flux isothermal evaporation technique.[6] Alternatively, proton inserted $Ba_6Mn_{24}O_{48}$ whiskers were used. To prepare the H-form of $Ba_6Mn_{24}O_{48}$ whiskers, the original whiskers were held in concentrated nitric acid for seven days at room temperature.[7] The composite materials were obtained by mixing a $V_2O_5{\cdot}nH_2O$ gel with the whiskers for two hours with periodic ultrasonic treatment (three times for 25 min). The sonication was used to distribute uniformly single reinforcing whiskers in the V_2O_5 gel. The gel/whiskers mixtures were dried at ~50 °C for 8 h in polystyrene cuvettes to produce composite films with a thickness of ~30–40 μm.

The mechanical strength of composite materials was evaluated using a tensile-testing machine with a highly sensitive tensor-measuring dynamometer, an elongation sensor and a stress transmitter. The measured values were recorded and processed using the tensor-measuring station Spider 2.0. The incoming signal was processed and scaled to F/L values, where F is the force and L is the elongation. The mechanical strength of composites containing 0, 20, 30, 50 and 80 wt% of $Ba_6Mn_{24}O_{48}$ whiskers was determined.

The electrochemical performance of $Ba_6Mn_{24}O_{48}$ whiskers and/or V_2O_5 xerogel-based materials was tested in model primary alkaline cells using a potentiostat (Ellis, PS-7M, Russia) with a constant load of 110 Ohm. A commercial positive electrode material (Camelion battery) and conventional MnO_2 powder with pyrolusite structure (pure for analysis) were electrochemically tested for a comparison with experimental samples. To assemble the cells, 30 mg of all the materials except for 30 mg of the battery cathode material were mixed with 20 wt% of graphite. Powdered zinc was used as a negative electrode. A 9 M KOH solution in dimethyl sulfoxide (DMSO) served as a liquid electrolyte since in contrast to aqueous KOH solution it does not cause swelling or degradation of V_2O_5 xerogel. Cellulose membranes (~200 μm thick) separated the areas of positive and negative electrodes.

The morphology of V_2O_5-based composite films was studied using a Nikon Eclipse E600 POL optical microscope and a Supra 50VP (LEO) scanning electron microscope with a WDX analyzer INCA Energy+ (Oxford). XRD analysis was performed in the 2θ range of 15–70° with a step of 0.03° (Dron 3M, Russia).

Figure 1(*a*) shows a typical optical micrograph of as-prepared V_2O_5 xerogels containing 30 wt% of $Ba_6Mn_{24}O_{48}$ whiskers. The whiskers demonstrate a cross-linking microstructure being effective for materials strengthening. XRD spectrum [Figure 1(*a*), inset] proves that $Ba_6Mn_{24}O_{48}$ whiskers do not affect the layered xerogel structure observed in the original xerogel films. The composite with 80 wt% of the whiskers [Figure 1(*b*)] looks like a bird's nest where bunches of the $Ba_6Mn_{24}O_{48}$ whiskers are glued together with xerogel. According to EDX microanalysis, the surface of films is composed of V and O atoms only confirming the chemical purity of the samples and the absence of chemical interaction of components of the composite.

The tensile strength experiments were carried out for composite materials with different $Ba_6Mn_{24}O_{48}$ whisker content. Figure 1(*c*) shows the fragments of whisker-reinforced xerogels after mechanical tests. The deformation energy leads to breaking xerogel into pieces and pulling the whiskers out of them, the latter facilitates energy dissipation and thus restrains the composite destruction [Figure 1(*c*)]. The change in mechanical properties with respect to $Ba_6Mn_{24}O_{48}$ whiskers content in xerogels is plotted in Figure 2. As can be seen, the tensile strength is maximal for a composite with ~50 wt% of the whiskers.

Figure 3 shows a comparison of the discharge curves for Zn–'MnO_2' cells to the end voltage of 0.3–0.4 V. The initial

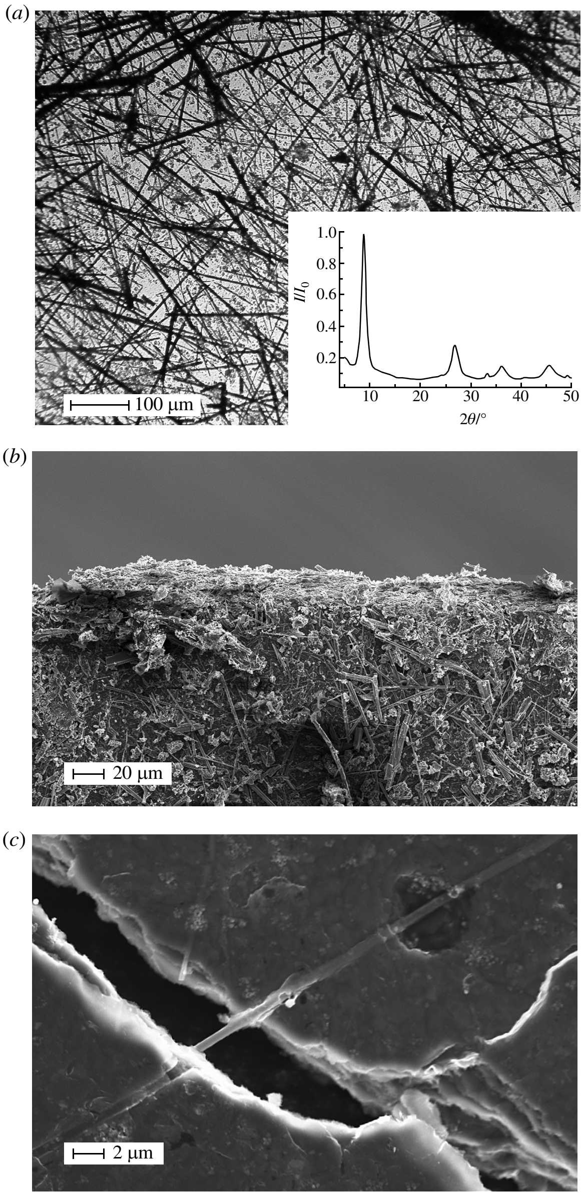

Figure 1 A typical view of V_2O_5 xerogels reinforced with $Ba_6Mn_{24}O_{48}$ whiskers: (*a*) optical microscopy, 50×, 30 wt% of the whiskers, the inset shows an XRD spectrum of $Ba_6Mn_{24}O_{48}$ whiskers-reinforced V_2O_5 xerogels; (*b*) SEM, 80 wt% of the whiskers; (*c*) crack development perpendicular to the whisker for a sample after mechanical tests.

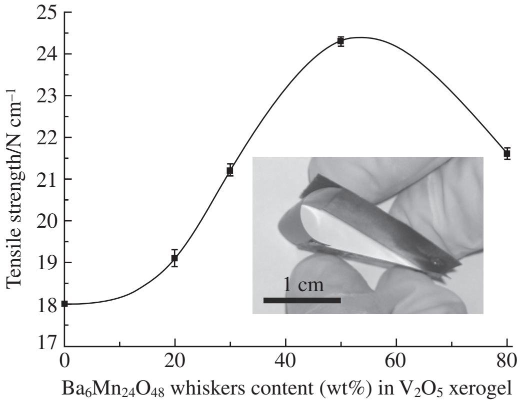

Figure 2 Tensile strength of the V_2O_5 xerogels containing different amounts of $Ba_6Mn_{24}O_{48}$ reinforcing whiskers; the inset shows a gneral view of the bent composite electrode material, the entire section of the composite is attached to a copper foil by glue. The sample in the inset is bended by fingers.

potential was 1.1–1.5 V depending on the electrode material and the voltage decreased gradually during the discharge process. MnO_2 does not exhibit any plateau on the discharge curve meaning a very low capacity and poor performance [Figure 3(*a*)]. The commercial cathode material, both original and protonated $Ba_6Mn_{24}O_{48}$ whiskers, exhibit discharge curves with a similar shape characterized by plateaus with average voltages of 0.6, 0.55 and 0.45 V, respectively. These values are lower than usually reported for similar systems[8,9] which might be due to the use of DMSO instead of aqueous KOH. The cells with original/protonated $Ba_6Mn_{24}O_{48}$ whiskers as cathode active materials exhibit a longer discharge plateaus than the cell with the commercial cathode material. The best electrochemical performance is shown by the H-form of $Ba_6Mn_{24}O_{48}$ whiskers originating from a higher surface area and the presence of structural defects[10] providing a more effective contact with the electrolyte and favoring diffusion. The comparison of electrochemical performance of the H-$Ba_6Mn_{24}O_{48}$ whiskers with that of V_2O_5 xerogel and composite materials is shown in Figure 3(*b*). The discharge curves have similar shapes; however, V_2O_5-based electrode materials exhibit lower characteristics compared to protonated whiskers. The plateaus become shorter and the average plateau voltage drops down to 350–400 mV, which can be due to the lower hydrogen intercalation capacity of V_2O_5 compared to $Ba_6Mn_{24}O_{48}$ whiskers. Thus, we found that the addition of H-$Ba_6Mn_{24}O_{48}$ whiskers significantly improves not only the mechanical strength of V_2O_5 xerogel but also its electrochemical performance.

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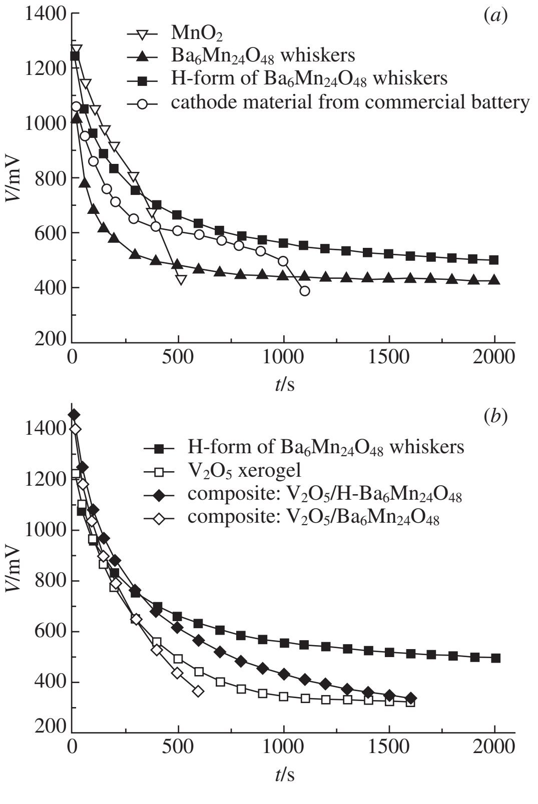

Figure 3 Comparison of the discharge performance of the model Zn-‘MnO_2’ electrochemical cells with a constant load of 110 Ohm (25 °C, a first discharge cycle); (*a*) manganese oxide-based cathode materials; (*b*) modified cathode materials (30 mg of an active cathode material were used in each experiment).

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