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# Impedance spectroscopy study of lithium ion diffusion in a new cathode material based on vanadium pentoxide

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Lithium intercalation and extraction were carried out in conventional tightly sealed Teflon cells. Xerogel-based cathode mass for working electrodes was prepared by mixing 75 wt% of $V_2O_5$ xerogel, 20 wt% of acetylene black (AB) and 5 wt% of a binder (polyvinylidenedifluoride dissolved in acetone). $V_2O_5$ xerogel/CNT cathode mixture was prepared by a similar procedure but with no AB added since CNT served as a conductive additive in this case. Cathode mixtures were sonicated for better homogenization and spread onto the 0.05 mm thick stainless steel grid. Electrodes were dried in the oven at 80 °C for 5 h followed by pressing under a load of 500 kg·cm$^{-2}$ for 30 s. Thus obtained square electrodes (1.5·1.5 cm$^2$) were kept at 240 °C in a vacuum for 20 h to remove remaining water traces. The typical quantity of an active material was 7–20 mg per electrode. Metallic lithium was used as counter and reference electrodes.

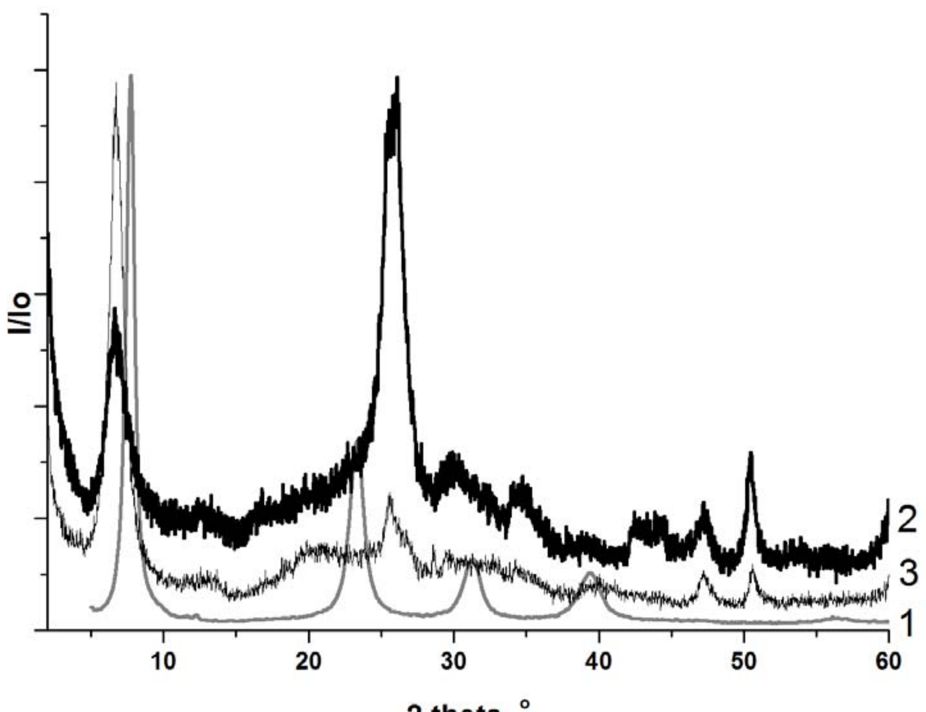
Hermetically sealed Teflon cells contained a working electrode, a counter electrode and a reference electrode. All electrodes were separated by a porous polypropylene membrane (‘Ufim’, Moscow, Russia). The cells were assembled in a glove box filled with purified argon gas. A 1 M $LiClO_4$ solution in the mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) (7:3) was used as an electrolyte (‘Litii-element’, Saratov, Russia). The water content estimated using Fisher coulometric titration (KF 684 Metrohm) was < 50 ppm.

Cyclic voltamograms were registered using an Autolab PGSTAT 302 potentiostat (Ecochemie) with a scan rate of 0.10 mV·s$^{-1}$. Galvanostatic charge-discharge cycling was performed at 20 °C using a multichannel cycler (‘Booster’, St. Petersburg, Russia) in the potential range of 1.5–4.0 V with a current density of 20 mA·g$^{-1}$ that corresponds to 0.031–0.045 mA·cm$^{-2}$.

**Table 1** Equivalent circuit parameters estimated by fitting experimental impedance spectra.[a]

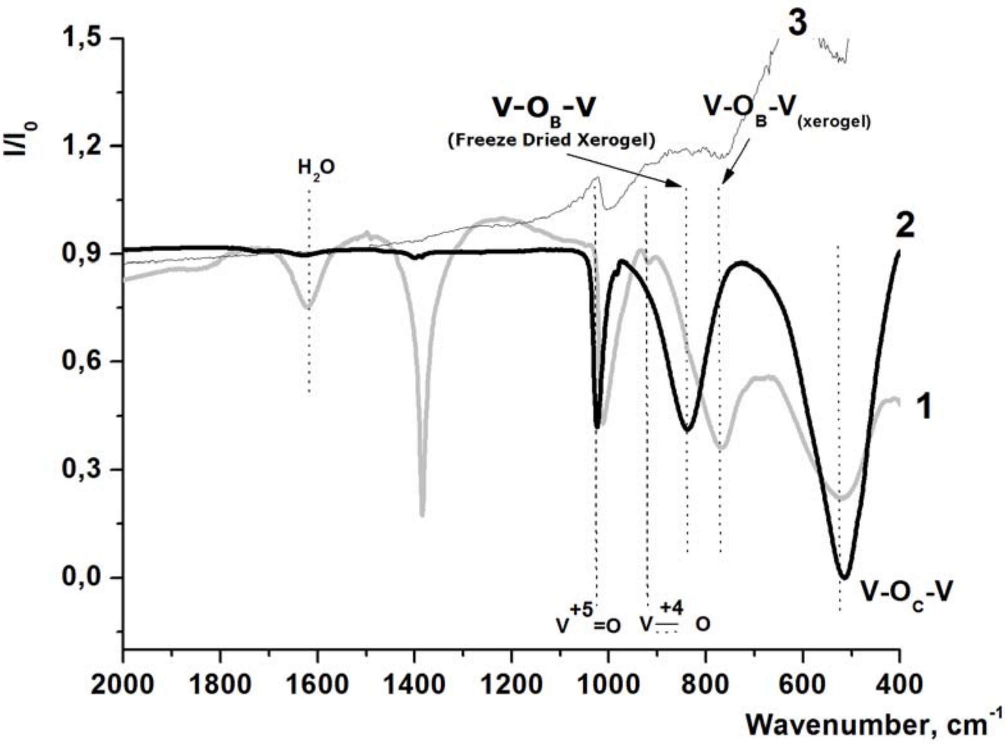
| Potential[b] | $R_e$/Ω | $R_{pf}$/Ω | $W_{pf}(C_{pf})$/F | $R_r$ /Ω | $C_{dl}$/F | $W_{ss}(C_{ss})$/F |
|---|---|---|---|---|---|---|
| $E_1^1$= 3.42 V | 1.6 | 1.70 | 0.0050 | 2.23 | 0.00030 | 0.01 |
| $E_2^1$= 3.20 V | 1.6 | 2.18 | 0.0010 | 3.47 | 0.00030 | 0.01 |
| $E_3^1$= 2.65 V | 1.6 | 2.58 | 0.0008 | 7.37 | 0,00028 | 0.08 |
| $E_4^1$= 2.43 V | 1.6 | 2.74 | 0.0009 | 8.30 | 0,00030 | 0.05 |
| $E_1^{100}$= 3.42 V | 2.0 | 2.28 | 0.0030 | 2.80 | 0,00030 | 0.05 |
| $E_2^{100}$= 3.20 V | 2.0 | 2.30 | 0.0010 | 3.50 | 0,00030 | 0.06 |
| $E_4^{100}$= 2.43 V | 3.0 | 3.10 | 0.0020 | 9.64 | 0,00080 | 0.06 |

[a] The equivalent circuit parameters abbreviations are explained in the caption of Figure 2.
[b] Superscript '1' denotes the estimated values corresponding to the first lithium intercalation/deintercalation cycle; superscript '100' denotes estimated values corresponding to the 100th lithium intercalation/deintercalation cycle (except for the potential $E_3$ = 2.65 V).



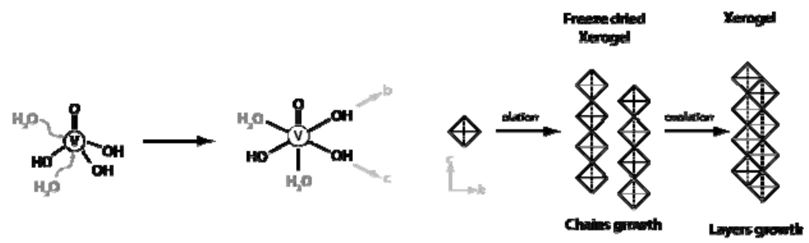

**Add. Figure 1** XRD patterns of the (1) $V_2O_5$ xerogel dried in conventional way, (2) freeze-dried $V_2O_5$ xerogel, and (3) freeze-dried $V_2O_5$ xerogel/CNT composite.

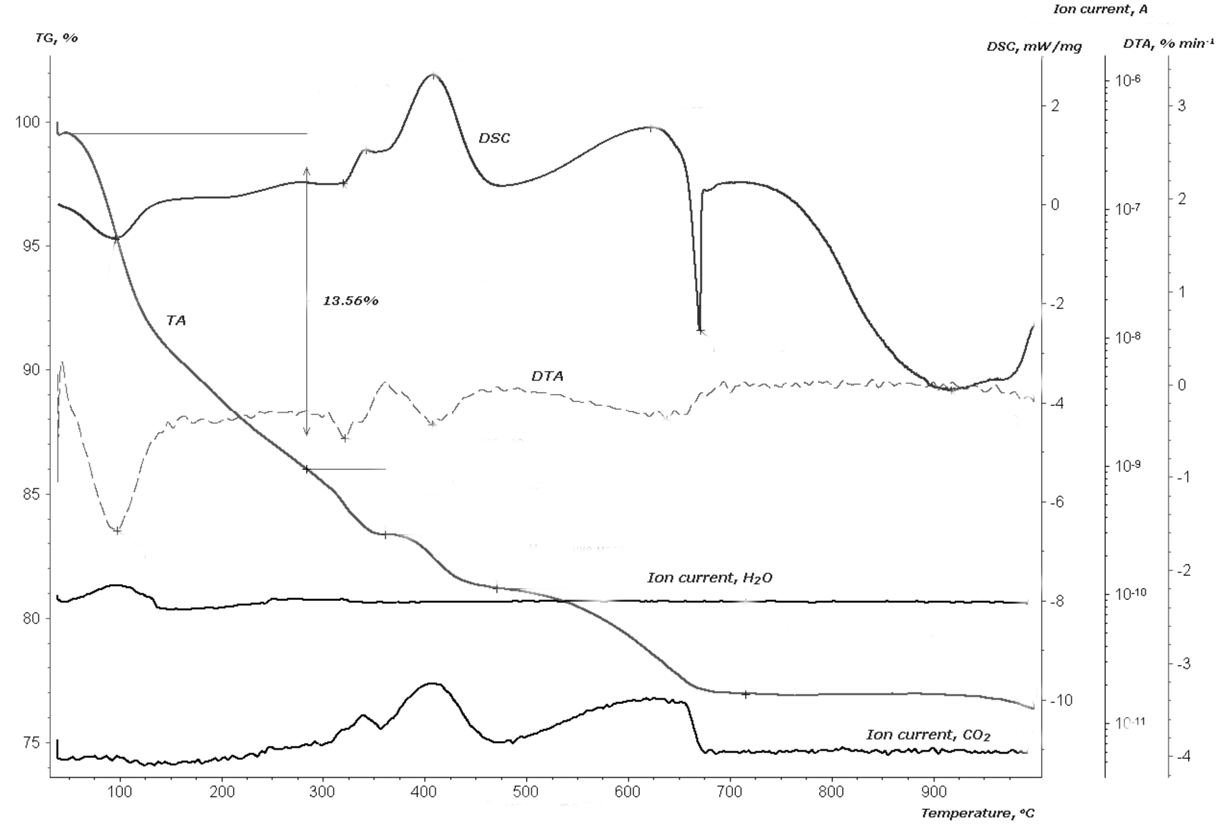
XRD data indicates that the layered structure characteristic of $V_2O_5$ xerogel dried in conventional way remains for the freeze-dried $V_2O_5$ xerogel and freeze-dried $V_2O_5$ xerogel/CNT composite.




**Add. Figure 2** The IR spectra of the (1) $V_2O_5$ xerogel dried in conventional way, (2) freeze-dried $V_2O_5$ xerogel, and (3) freeze-dried $V_2O_5$ xerogel/CNT composite.

The main bands in the IR spectra characteristic of $V_2O_5$ xerogel at 1610, 1006, 758 и 531 $cm^{-1}$ correspond to the following vibrations: δ(H–O–H), ν(V=O), *ν* ($V^{+5}$=O), δ(V–O–V) и δ(V–O). The small band at 975 $cm^{-1}$ can correspond to the *ν*($V^{+4}$=O) vibrations. The band at 1384 $cm^{-1}$ correspond to the $NO_3^-$ admixture in KBr. The frequencies of the main adsorption bands are in the agreement with the literature supporting the expected structure of the as-synthesized xerogels. The change in the V-$O_B$-V vibration can be related to the method of $V_2O_5$/CNT composite synthesis (freezing in liquid nitrogen occurred on the early stage of the oxolation process affecting the energy of V-$O_B$-V bond, see figure below). The presence of carbon nanotubes in the composite material causes the strong absorption resulting in a poor quality of the IR spectrum.






**Add. Figure 3** Thermal analysis (weight loss, DTA and DSC curves) of freeze-dried $V_2O_5$ xerogel/CNT composite. Signals corresponding to evolving water vapour and carbon dioxide are based on chromatomass-spectroscopy of evolving gases.

The water content and electrodes drying conditions were estimated using thermal analysis data with mass-spectroscopy of evolving gases. It was shown that at 240$^o$C carbon nanotubes do not oxidize forming $CO_2$. At the same time at this temperature (240$^o$C) a minimum water content in the active electrode material is achieved. Thus, this temperature was selected for electrodes drying before electrochemical tests.