Surface functionalization of nanostructured vanadium pentoxide for lithium-ion batteries applications

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Nowadays, research aimed at improving the performance of lithium batteries (LiB) have been increasing, since the demand for energy storage is expected to grow 300% by 2030 [1]. Particularly, research is focused on enhance the charge/discharge capacity, efficiency, and lifespan, where the cathode of batteries is of great relevance, since the battery performance critically depends on it.

The most commonly used cathodes for LiBs are $LiMn_xNi_yCo_zO_2$ in hybrid or electric vehicles and $LiCoO_2$ in other small devices such as cellphones. However, V_2O_5 has attracted much attention due to its high theoretical charge capacity (294 mAh/g) [3]. For this reason, it is expected to improve the stability of this material in battery testing and several strategies have been developed, among which the surface coating stands out to prevent the reduction action of the electrolyte [4].

In this work, V_2O_5 thin films were fabricated and functionalized with two different molecules, 4-aminobenzoic acid (PABA) and 4-phenylazobenzoic acid (PPBA). The samples were characterized by atomic force microscopy (AFM), conductive AFM (C-AFM), and angle resolved x-ray photoelectron spectroscopy (AR-XPS). Therefore were tested as cathode for lithium-ion batteries and afterwards it was made a postmortem analysis. Additionally, density functional theory simulations (DFT) were performed to compare with the experimental results.

The chemical composition of the surfaces was mainly V^{+5} with a low proportion of V^{+4} oxide state in a ratio V^{+5}:V^{+4} close to 8:1 for the bare surface, and the proportion increases close to 24:1 when functionalizing with molecules. Furthermore, the topography of samples presents disk-shaped structures with atomically flat terraces connected throw seps, typical of laminar materials, also the molecules does not affect in roughness. Moreover, the terraces present higher conductivity than borders and the functionalization with molecules just increases that difference by increasing the conductivity in terraces and lowering it in the step. By comparing XPS results with DFT simulation, it was concluded that the molecules form a self-assembled monolayers (SAMs) onto vanadium pentoxide surfaces. Additionally, the bare and PPBA capped samples were tested as cathode for lithium-ion batteries. The oxidation and reduction peaks of vanadium pentoxide were observed, afterwards in cyclability measurements it was observed that PPBA capped V_2O_5 presents a higher charge/discharge capacity and also higher coulombic efficiency, probably due to the increase in electronic conductivity through the terraces. After battery testing, the vanadium pentoxide cathodes were disassembled and analyzed by XPS, where it was observed a reduction in degraded lithium salts concentration compared to HF in the surface, accompanied by an increase in the total Li_2CO_3 concentration in the PPBA capped surface, which may indicate the formation of a protective CEI by the presence of the molecule.

Acknowledgments

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References

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