

# THE ELECTROCHEMICAL LITHIUM INSERTION PROPERTIES OF A NEW VANADIUM OXYFLUORIDE WITH $\text{ReO}_3$ -TYPE STRUCTURE

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Transition metal (TM) fluorides have been investigated in the search of new chemistries for lithium ion rechargeable batteries. In spite of the characteristic insulating behavior of these typical ionic compounds they are highly interesting. Fluorine ligands tend to raise intercalation potential opening new possibilities to find high energy electrode materials. However, the increment of intercalation potential with respect to similar oxides may drive the operating window out of the electrochemical stability window of the commonly used liquid electrolytes. A controlled effect on potential increase may be reached through the partial substitution of oxygen by fluorine. Thus proper oxygen by fluorine substitution may produce an increase of the intercalation potential but keeping it below the high voltage stability limit of the electrolyte. An important drawback is that stoichiometric control is not easily achieved and the chemistry of oxyfluorides is not as well-known as the chemistry of oxides. Academy has to make an effort to develop basic knowledge on these interesting materials and in particular reliable, reproducible and safer (HF free) synthesis methods. Note that due to crystal chemistry differences between oxygen and fluorine, crystalline structures with different features for insertion reaction may exist.

In this connection we have been working in the past few years on cryolites  $\text{Li}_3\text{MF}_6$  ( $\text{M}=\text{Fe}$  and  $\text{V}$ ) and in the partial substitution of  $\text{F}$  by  $\text{O}$  which it proved to be difficult. However, we contribute now to the research on oxyfluorides by presenting a new oxyfluoride  $\text{VO}_2\text{F}$  for which non previous evidences of its existence had been reported. It fills the gap in the  $\text{MO}_2\text{F}$  compounds of Group 5 elements:  $\text{V}$ ,  $\text{Nb}$  and  $\text{Ta}$ . Intercalation of lithium into  $\text{NbO}_2\text{F}$  has been reported, but vanadium is much more interesting owing to its lightness.

The synthesis procedure consists in simultaneous high temperature and high pressure treatment of  $\text{V}_2\text{O}_5$  and  $\text{VF}_3$  mixture at 4 GPa and 1073K. Vanadium dioxyfluoride is isostructural with  $\text{TiO}_2\text{F}$  exhibiting a hexagonal structure related to the  $\text{ReO}_3$  structure.

A complete chemical and microstructural study has been undertaken to fully characterize the new oxyfluoride. Regarding its electrochemical behavior, it is characterized by a long discharge from 4 to 1.5 V that develops ca. 450 mAh/g. However, the voltage-composition curve during the whole first discharge – charge cycle and further cycling (reversible capacity of 350mAh/g) indicate that  $\text{VO}_2\text{F}$  transforms irreversibly, similarly to the case of  $\text{NbO}_2\text{F}$ . In the high voltage region a kinetically limited intercalation reaction takes place. Mechanical milling enables intercalation and thus a reversible capacity of 250 mAh/g has been observed in the 4-2.25 V range. Nevertheless cycleability has been found to be limited in the high voltage region. Changes of vanadium oxidation state upon intercalation are presently being investigated by XAS to shed light in the intercalation reaction mechanism.