

CONTROLLED MIXED VALENCIES IN 2D SYSTEMS: ZrSe_y and Fe-GIC.

R. YAZAMI

Laboratoire d'Ionique et d'Electrochimie du Solide de Grenoble
URA-CNRS 1213, ENS. d'Electrochimie et d'Electrometallurgie de
Grenoble, INPG, BP 75, 38402 St. Martin d'Heres, France.

There exists two main routes to modify, or to a certain extent to control mixed valencies of a transition metal contained in 2D-materials : 1) by good control of the synthesis conditions and 2) by modifying the internal charge balance consecutive to the intercalation into the 2D host structure of chemical species able to act as electron donors or acceptors. In this paper we show these two effects through two types of 2D systems: zirconium diselenide (ZrSe_y) and GIC with some metal chlorides.

1) Synthesis conditions

1-a) ZrSe_y :

This compound is non-stoichiometric whatever are its synthesis conditions, being always deficient in Se. Its existing domain of stoichiometry is $1.85 < y < 1.95$, therefore the charge balance should be realized by the appearance of state valency of Zr lower than 4, very likely 3, under the assumption that the selenium is essentially Se^{-2} . The ratio $\text{Zr}^{3+}/\text{Zr}^{4+} = z/1-z$ where $z = 4 - 2y$ can be fixed by the elements ratio (Zr:Se) introduced into the reactor prior to the synthesis. The reaction temperature, its duration and the successive mechanical (grinding) or thermal treatments of the powder also play important role in the final compound stoichiometry. Depending on the departure from stoichiometry, ZrSe_y behaves as a semi-conductor ($1.90 < y < 1.95$) or as a metal ($1.85 < y < 1.90$), and this composition induced transition has been extensively studied by the French group at Nantes and Grenoble Universities.

1-b) GICs with metal chlorides

The effects of the graphite origin, the synthesis reaction temperature and the partial pressure of chlorine on the final GIC composition and stage are particularly important. We have showed that a high filling factor of 90% can be reached in the stage-1 GIC with CoCl_2 . This affects the magnetoelastic properties of this material which exhibits a huge magnetostriction in high fields. In the case of GIC-NiCl_{2+x} , the stage-1 compound was prepared at high temperature and high chlorine pressure (10 atm. at 700 C). The excess of chlorine x is directly related to the partial pressure of chlorine in the vapor phase. NiCl_2 is believed to form discontinuous domains or islands in which excess chlorine should be located at the external frontiers. Therefore, in this model, the average size of the islands decreases with x . However, in our sample x was found as high as .35 which should lead to islands of around 30-50 Å. High resolution electron

microscopy did not allow us to observe such small islands, so we do not exclude the existence of Ni^{2+} vacancies within the NiCl_2 domains. Such vacancies should be consecutive to the appearance of Ni^{3+} state and should modify the characteristic temperature in the susceptibility measurements. In the FeCl_3 -GIC, the chlorine gas plays a major role in the vapor phase equilibrium in which FeCl_2 is formed as consequence of a thermal decomposition of FeCl_3 . The charge transfer between FeCl_3 and graphite implies a lower amount of Fe^{2+} when a high pressure of chlorine is used.

2) Intercalation induced mixed valencies:

2-a) Li_xZrSe_y :

We have showed that the electronical properties of the host ZrSe_y play important role in the conditions of the electrochemical intercalation of lithium in solid state cells i.e. when a semi-conducting material is used, lithium first occupies sites near the selenium vacancies which are the predominant nature of departure from stoichiometry. In this step, there occurs no increase of the lattice parameter I_c along the c-axis. The second sites of lithium are the normal octahedral ones in the van der Waals gap, and the intercalation is followed by an increase of I_c . There, a transition from the semi-conducting to metallic state occurs with increasing charge transfer. In the metallic like host, the lithium intercalation occurs at lower potential than in the previous semi-conducting case due to higher amount of defects found in the host. In addition to selenium vacancies, some interstitial Zr is present in the ZrSe_2 layer, so broader peaks in the cyclovoltammograms are observed contrasting with the fine and well located ones found with the semi-conducting host.

2-b) $\text{C}_n\text{Li}_x\text{FeCl}_3$:

The chemical reduction of stage-1 GIC with FeCl_3 by butyllithium in hexane solution allowed us the study of the progressive decrease of the Fe valency from 3 to 2 and to 0. This was carried out by the crystal, Mossbauer and magnetic measurements as function of the amount x of intercalated lithium. When $x=1$, there was no strong change in the I_c value in comparison with that of the parent GIC. The Mossbauer spectrometry revealed that 80% of Fe was reduced from 3+ to 2+. A new phase appeared when $x=2$ consisting of a Fe^0 -GIC of stage 1, with $I_c=5.44$ A, much more lower than that of the FeCl_3 -GIC ($I_c=9.36$ A). Mossbauer also showed the presence of Fe^0 beside Fe^{2+} and lower amounts of Fe^{3+} . The ferromagnetism is also enhanced. In the $x=3$ compound, the X ray diffraction showed that the main phase consisted of a stage-1 Fe-GIC in which Fe forms a hexagonal superlattice incommensurate with that of graphite ($a=4.15$ A and $c=10.88$ A). A spin glass behavior with strong ferromagnetic interactions is also found. Mossbauer revealed two types of Fe^0 sites whom characteristics differ from that of Fe metal. The formation of small size metal clusters is not excluded even though their detection by X ray diffraction was not possible.