LAYERED $LiNi_{1-x}Al_xO_2$ AND $LiCo_{1-x}Al_xO_2$ THIN FILMS AS ELECTRODE MATERIALS FOR ELECTROCHROMIC DEVICES

F. Svegl* and B. Orel+

*ZAG - Ljubljana, Dimičeva 12, SI-1000 Ljubljana, Slovenia

+National Institute of Chemistry, Hajdrihova 17, SI-1000 Ljubljana, Slovenia

Layered $LiNi_{1-x}Al_xO_2$ and $LiCo_{1-x}Al_xO_2$ (where $0.02 \le x \le 0.2$) thin films with rhombohedral ($R\bar{3}m$) structure were prepared by wet chemistry route from Li(I), Co(II), Ni(II), and Al(III) salt precursors [1]. The formation of small uniform polycrystalline particles (below 100 nm) enables interesting electrochemical behavior of materials which were studied by cyclic voltammetry (CV), galvanostatic intermittent titration (GITT) and some other potetiostatic and galvanostatic techniques in a 1M $LiClO_4$/propylene carbonate electrolyte solution. Structural changes in materials, which appeared during (de) intercalation of Li^+ ions, were investigated with XRD and FTIR spectroscopy.

Study of as-synthesized materials showed that in the region of higher potential than 4.2 V for $LiCoO_2$, a capacity fading owing to cobalt dissolution was diminished with the Al^{3+} doping of $LiCo_{1-x}Al_xO_2$ ($0.02 \le x \le 0.20$) structure. XRD analysis reviled prolongation of c-axis and shortening of a-axis of hexagonal unit cell with the increase in Al^{3+} doping of $LiNi_{1-x}Al_xO_2$ and $LiCo_{1-x}Al_xO_2$ materials. The amount of intercalated lithium ions decreased with increasing Al content, which resulted in lower charge capacities (120 mAh g^{-1}). The galvanostatic measurements showed that over 2/3 of Li^+ ions be reversibly removed from the structure of $LiNi_{1-x}Al_xO_2$ and $LiCo_{1-x}Al_xO_2$, respectively. All the compounds showed an irreversible capacity loss between the first charge and discharge. The lowest loss of only 18 mAh g^{-1} was observed for $LiNi_{0.97}Al_{0.03}O_2$ electrodes. A diffusion of Li^+ ions in the structure of layered $LiNi_{1-x}Al_xO_2$ and $LiCo_{1-x}Al_xO_2$ during (de)intercalation step was a slow process ($D_{Li+} \approx 10^{-10} - 10^{-14}$ cm^2 s^{-1}), approximately linearly dependent on stoichiometry of the materials. The chemical diffusion coefficient, D_{Li+}, in $LiCo_{1-x}Al_xO_2$ electrode was of the order of 10^{-14} cm^2 s^{-1} at room temperature, which is one order magnitude higher than that for $LiCoO_2$. The obtained values decreased with the intercalated Li^+ content, δ.

The (de)intercalation process is accompanied by the coloring/bleaching of thin films deposited on ITO substrate. Both types of films showed stable electrochromic response in the range between 2.5 and 4.2 V vs. Li/Li^+ electrode with the total change in transmittance of about 60%. Films were tested as active counter electrodes in the electrochromic devices, containing amorphous WO_3 electrochromic film and polymer Li^+ electrolyte [2].

References

1. F. Svegl, B. Orel, J. Sol-gel Sci. Technol., 14 (1999) 187.
2. F. Svegl, B. Orel, V. Kaucic, Sol. Energy. 68 (2000) 523.