Cycling Capacity of Electrochromic Cells

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The performance is actual problem of electrochromic coatings. The service and shelf life and cycling capacity are main performance characteristics. By solid-state ionics point of view any electrochromic cell based on phenomena with ion insertion – extraction processes is functioning as solid-state rechargeable battery. The main performance characteristics of electrochromic cells as service and shelf life and cycling capacity (CC) will be similar to batteries.

The CC of electrochemical battery cells depend on charge and discharge intensity, i.e., charge and discharge current. For EC cell it means coloration intensity or value of induced optical density $\Delta D \sim \Delta Q$. The B.W.Faughnan and R.S.Crandal [1] experimentally found relation between number of cycles N and fixed value of contrast K as $\log N = \log N_{max} - \gamma \log K$ or $NK^{\gamma} = N_{max}$=const, where $\log K = \Delta D$, $\gamma = 3.3$ and $N_{max} = 10^7$ can be defined as CC for EC cell based on amorphous WO_3 film. This relation connects ion insertion, i.e., charge and discharge reactions, and degradation processes in the EC cell. In this relation value $\delta = K^{\gamma}$ can be interpreted as loss function of active tungsten ion sites (loss of color centers) for reversible coloration during one cycle.

In this paper will be analyzed performance problems of ECC based on a-WO_3 films and protons conducting electrolyte. Our basic investigations of cycling capacity had been done on the EC cells based on multi layer system on glass substrates:

ITO / WO_3 // AAH // IrO_2 / ITO,

where WO_3 and IrO_2 are represented hydrated oxide films, AAH – electrolyte as paste or gel based on hydrate of antimony acid. The a-WO_3 films were prepared by thermal evaporation of tungsten trioxide powder in the presence of H_2O vapors.

We are developing model of electrochromic phenomena in tungsten oxide thin films based on assumption that the constitution of such films is heterogeneous and built up of nano size particles, pores and adsorbed substances (mainly water) [2]. From electrochemistry point of view the internal three phase interfaces in such films are distributed multiphase electrodes.

The changes of characteristics of ECC have to be related to degradation of them as electrochemical system. The CC of ECC depended on degradation intensity, which can be controlled by coloration intensity. During storage and cycling for any characteristic have to be distinguish three regions of degradation intensity (Fig.1): stabilization, durability and drop down. The full cycling region is cycling capacity, which depends on reversibility of electrode reactions of ion insertion or phase stability of electrode and electrolyte materials.

During cycling of ECC the migration of H_2O and H_3^+O or other chemical species and phase transformations are going on. The changes of physical and chemical state of EC electrode material and interface electrode-electrolyte are related to degradation processes.

The first stage (up to 10^6 cycles and up to two years storage) involves the migration of H_2O in electrolyte and WO_3 layer. After 10^6 cycles or 3 years storage hydration of the WO_3 is the dominant phenomenon and after 10^7 cycles WO_3 separates from the ITO layer. The migration of water in the cell and hydration together with ion insertion-extraction reactions of the WO_3 film have main role in formation of new phases, which determine the value of cycling capacity. The cycling capacity at constant coloration intensity is limited by initial total number of active tungsten ion sites for induced color centers at inner surface of porous WO_3 film.

The more probable transformation of phases in hydrated WO_3 films during cycling, which can be related to loss of active tungsten ion sites, is transformation of octahedral structural units of $H_xWO_3 \cdot nH_2O$ to tetrahedral $H_2WO_4 \cdot mH_2O$.

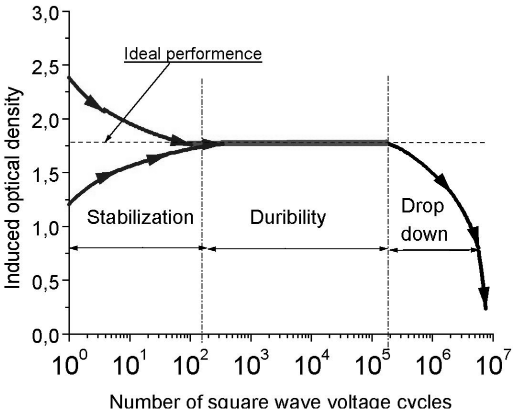

Fig.1 ECC performance – degradation scheme

1. B.W.Faughnan, R.S.Crandal: Electrochromic Displays. In book edit. by Pankov J.I.: *Displey Devices. Topics in Applied Physics*, **40**, Springer-Verlag, New York, 1980.
2. .A.Lusis, *SPIE Proceedings*, **2968**, p.167-173, 1997