SPECIFICATION OF REDOX PROCESS PART IN ELECTROCHROMISM OF LANTHANIDE DIPHTALOCYANINES

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Diphtalocyanines of rare-earth have been synthesized for the first time in 1964 in LNPI, the USSR Academy of sciences /1/ to obtain enriched radioactive isotopes according to Szilard-Chalmers method /2/.

Semiconductor crystals of these compounds were found to have unusual physical and chemical properties. They revealed effects of mechanothermochromism /3/ and electrochromism /4/. The last effect receives a great interest from researches due to the possibility to create electrically directed light filters /5/ and indicators /6/ based on it.

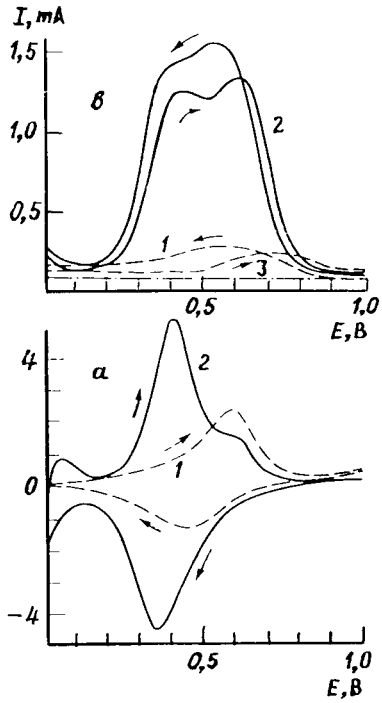

Fig. 1

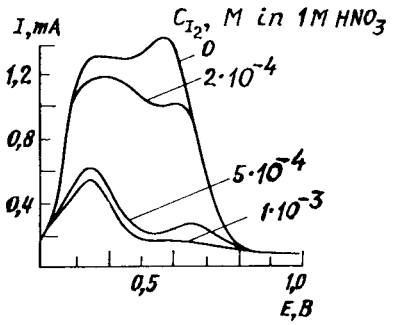

Fig. 2

By the time we began the present work the effect of oxidation and complex formation with electron acceptor molecules has been detected in lanthanide diphtalocyanines (LDP) anode electrochromism. But the details of the two processes relationship were still obscure. Our work was aimed to obtain additional experimental data on relative part of the two processes using traditional method of cyclic voltammography (CVA), with registration of electromagnetic induction spectrum (EIS), i. e. a new version of classical method of electrochemical impedance /7/. EIS was registered with CVA complex designed in the Institute of Electrochemistry, the USSR Academy of Sciences. We have supplied it with a capacitance filter and a rectifier on input of two-coordinate recorder. A coil with axis parallel to electrode planes provided alternativ magnetic field in a cell with 50 Hz frequecy and the amplitude from 0.5 to 5 Oersted.

Working electrode potential was measured relative to standard silver chloride electrode. Films of oxidized forms of LDP about 100 nm thick were applied to a smooth platinum surface of the electrode. EIS were registered when CVA-curves at slow cycle change of working electrode potential with a rate up to 5 mV/s have come to the stable form.

Fig. 1 shows dependence of CVA (*a*) and EIS (*b*) for a film of oxidized form of lutetium diphtalocyanine in the region of colour change potentials (green to brown) in neutral (1M KNO — solution 1) and acid (1M HNO — solution 2) media. Arrows denote the direction of potential change. Dashed line characterises the background dependences. H is 5 Oe, rate of electrod potential change is 5 mV/s. One can see from the figure considerable difference between the curves for neutral and acid media. Quantitative comparison of CVA peak areas allows to assume that only about half of a substance on an electrode is involved into a redox process, the rest part of it being transformed into charge transfer

complexes with, for example, oxygen dissolved in water. Such a reaction also takes place in acid medium, which is confirmed by the fact that the increase in concentration of iodine electron acceptor molecules results in complete suppression of the second peak in EIS (fig. 2, H=5 Oe, v=5 mV/s). Therefore the chemical reaction is peculiar for the second stage of the green form oxidation into the brown one.

We have obtained analogous results for all LDP as well as for yttrium and scandium. The CVA and EIS are similar each other for the whole number of mentioned elements with small quantitative differences.

Appearance of EIS as a result of application of thin layers of LDP onto an electrode at such a low magnetic field suggests an idea about possible connection of the phenomenon with big diamagnetism of phtalocyanine ligand and can be used for further investigation of similar systems.

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