ELECTROCHEMICALLY FORMED TWO-COMPONENT FILMS OF FERROCENYLFULLERO[C_{60}]PYRROLIDYNE AND TRANSITION METAL COMPLEXES

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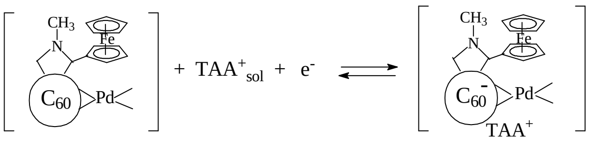
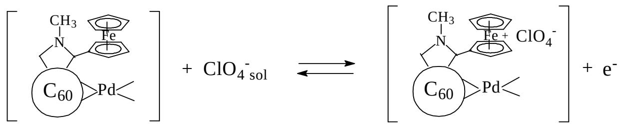
The investigations are focused at the study of the electropolymerization and the redox behavior of ferrocenylfullero[C_{60}]pyrrolidine/M (M = Pd, Pt, Ir, Rh) films. The aim of the work is to create a new redox-active fullerene-based polymer having both p- and n-doping properties due to the presence of electron-donating ferrocene and electron-accepting fullerene moieties. In this case, C_{60} moieties and transition metal atoms or complexes form a conjugated polymer backbone with ferrocene centers linked to it. Characterization of the polymer films was done by cyclic voltammetry, electrochemical quartz crystal microbalance, FT-IR spectroscopy and scanning electron microscopy.

Films are formed by the electrochemical reduction of ferrocenylfullero[C_{60}]pyrrolidine and transition metal complexes in toluene/acetonitrile (4:1, v:v) solution containing $[(n\text{-}C_4H_9)_4N]ClO_4$. *Fig. 1b* shows the ferrocenylfullero[C_{60}]pyrrolidine/Pd film formation. Examination of the electrode surface after multycyclic potential scanning reveals the presence of a black deposit. Film shows a grain-like surface structure as seen in *Fig. 2*. The surface is relatively uniform with densely packed grains.

The electrode covered with the ferrocenylfullero[C_{60}]-pyrrolidine/Pd film exhibits electrochemical activity both at negative and positive potentials (*Fig.1c*). The reduction of the film at negative potentials is due to the presence of fullerene centers in the main polymeric chain. Switching between oxidation states at negative potentials under voltammetric conditions results in broad peaks with high capacive current. Such behavior resembles the redox properties of typical conductive films such as polypyrole, polyaniline, or polythiophene. The reduction and reoxidation of the ferrocenylfullero[C_{60}]pyrrolidine/Pd film involves cation transport between the film and the solution:



The oxidation of ferrocene groups occurs at positive potentials. This process resembles behavior observed for other redox-polymers. The film oxidation peak is sharp and symmetrical. In contrast to the reduction process, the changes of film capacity associated with the oxidation process are much smaller. In this case, the electron transfer occurs via a process of sequential electron self-exchange between neighboring ferrocene groups. The charge percolation through the layer is accompanied by the anion transport between solution and the film according to the following reaction:



Depending on the film thickness and the sweep rate, the oxidation process can be controlled by the rate of electron transport (low sweep rate or thin film) or by the rate of ion transport (high sweep rate or thick film). The film exhibits higher permeability for the small perchlorate anions than large tetra(*n*-alkyl)ammonium cations. The oxidation process also results in substantial changes of the film structure.

Results presented in this paper open a field of study of other transition metal complex-ferrocenylfullero[C_{60}]-pyrrolidine systems which may produce redox active films. The structure and properties of the films may be tuned by varying the chemical structure of the spacers connecting fullerene moieties. The formation, structures and redox properties of this family of electrochemically produced films are under investigation.

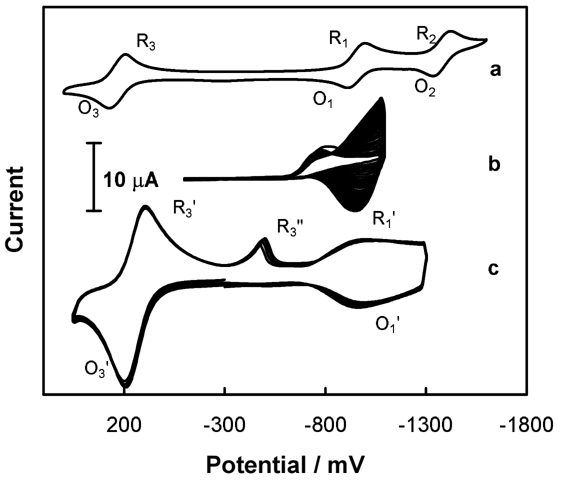


Fig.1. (a) Cyclic voltammograms obtained for 0.31 mM ferrocenylfullero[C_{60}]pyrrolidine in acetonitrile/toluene (1:4, v:v) containing 0.10 M $TBAClO_4$.
(b) Multicyclic voltammogram (20 cycles) obtained for 0.31 mM ferrocenyl-fullero[C_{60}]pyrrolidine and 0.55 mM $[Pd(ac)_2]_3$ in acetonitrile/toluene (1:4, v:v) containing 0.10 M $TBAClO_4$.
(c) Multicyclic voltammogram (4 cycles) of ferrocenyl-fullero[C_{60}]pyrrolidine/Pd electropolymerized film over the potential range from +500 to –1250 mV in acetonitrile containing 0.10 M $TBAClO_4$.

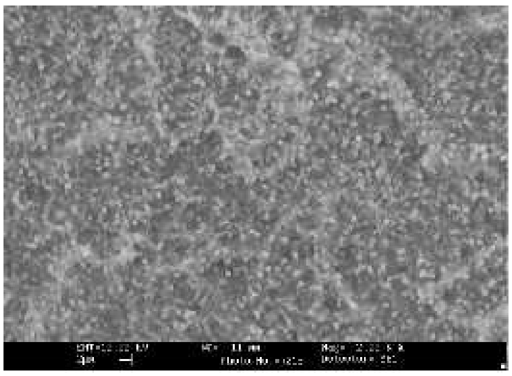


Fig. 2. SEM images of films formed on gold foil under cyclic voltammetry conditions (20 cycles) over the potential range from -200 to –1200 mV in acetonitrile/toluene (1:4, v:v) containing 0.31 mM ferrocenylfullero[C_{60}]pyrrolidine, 1.20 mM $[Pd(ac)_2]_3$, and 0.10 M $TBAClO_4$.