

## Charging Process of Conducting Polymers and Oligomers: Effect of Intermolecular Bond Formation

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The charging process in almost all conducting polymers during the cyclic voltammetry (CV) possesses a characteristic feature: its current is proportional to the scan rate while the anodic and cathodic branches show a pronounced hysteresis. Besides, the CV curve has got a specific shape, the combination of broad anodic and cathodic peaks with a plateau of the current at higher charging levels.

For a long time its interpretation has been given within the framework of the model of "polarons" and "bipolarons" although this hypothesis resulted in a contradiction to experimental evidences. The failure of this approach has become especially clear as a result of the CV studies of polyphenylene films (Fig 1) for various values of the anodic or cathodic limits of the potential sweep. These experiments have clearly indicated the existence of at least three different types of electronic species at the polymer matrix. Two of those species follow the potential variation in a *quasi-equilibrium* manner while the third entity is related to an *irreversible* transformation.

An indication on the possible type of the latter species is provided by recent studies of electrochemically induced redox processes in "conducting oligomers" (analogs of conducting polymers). It has been revealed that generated cation radicals  $R^{\cdot+}$  are subject to a rapid dimerization,  $R^{\cdot+}R^{\cdot+}$ , with formation of an intermolecular  $\sigma$ -bond which is broken during the cathodic sweep.

Based on these experimental evidences we have developed [1] a theoretical approach for the charging/discharging process in solid films of electron conducting polymers or oligomers. The shift of the electrode potential into the positive direction leads to a reversible generation of cation radicals at polymer (or oligomer) chains which are transformed into dication at higher charging levels. Besides, two cation-radicals located at favorable sites of neighboring polymeric chains are able to create an intermolecular bond. This process being strongly exothermic is retarded by the energetic barrier due to the necessity for the neighboring chains to approach each other at the short distance. Once the bond is formed its low energy prevents its break within the same potential range so that this charged component is only reduced at much more negative potentials.

Qualitatively, the theory attributes the anodic and cathodic peaks to the bond formation and its break so that the above reasoning explains a significant difference of their potentials (hysteresis) observed experimentally.

For the quantitative consideration, the set of kinetic equations describing the mutual transformations of free cation radicals and dication as well as dimerized species in the course of cyclic voltammetry has been analyzed numerically [1]. Its solution has provided an interpretation of the cyclic voltammetry curves of polyphenylene films

(Fig 1) with variable limits of the potential sweep. As a result, we have determined the crucial parameters of this polymer film during the charging/discharging process, potentials of radical cation and dication formation, energy of the intermolecular bond, kinetic constants for the bond formation and its break etc.

The same theoretical model has been successfully applied for the interpretation of CV data for solid films of conducting oligomers deposited at the electrode surface (Fig 2). The radical difference of the shape of voltammograms for these two groups of conducting materials has been attributed to a much higher concentration of the sites at the oligomer-film matrix where the dimerization can take place, as consequence of the more uniform structure of these systems (regular length of molecules, contrary to its wide dispersion in polymers).

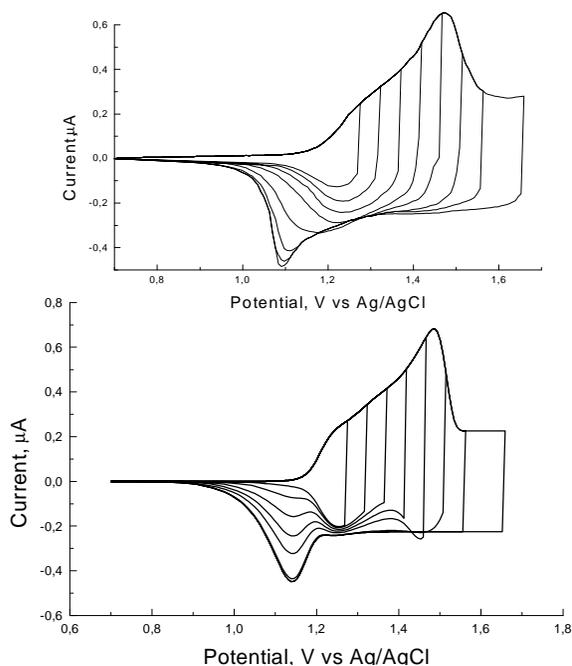


Fig. 1. CV of the polyphenylene film with a variable anodic potential limit,  $v = 100$  mV/s. Experimental data (above) and simulating curve (below).

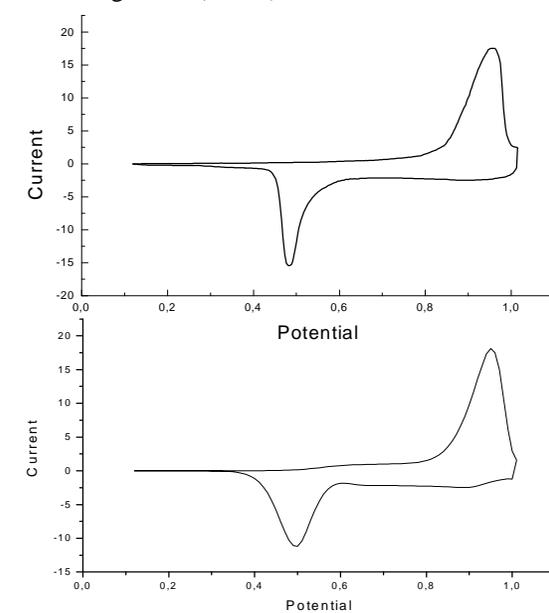


Fig. 2. Solid-state CV for the oligothiophene film ( $\alpha$ 8T) in  $\text{CH}_2\text{Cl}_2$  / TBAPF<sub>6</sub>,  $T = -5$  C,  $v = 10$  mV/s. Experimental data (above) and simulating curve (below).

### References

1. M. A. Vorotyntsev, J. Heinze, *Electrochim. Acta*, in press