Electroanalytical Screening Method for Characterization of Charge Transport Compounds

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Abstract

Cyclic voltammetry has been demonstrated as a rapid screening method for use in characterization of charge transport materials. This technique is simple, fast, and inexpensive to perform. The method provides information about electron transfer processes including band gap of the material and the relative ease of charge and discharge. Certain features of the cyclic voltammetric (CV) wave correspond to events involved in charge generation, charge transport, and discharge within the photoconductor. The potential of the first CV wave observed, either reduction or oxidation, corresponds fairly well to the ease of charging the photoconductor. The type of electron transfer indicates whether the material is more readily oxidized (to positive charge) or reduced (to negative charge). The current ratio of that CV wave is a reasonable predictor of the ease and completeness of discharge, and the reversibility of the wave is a predictor of the kinetics of the process. We report results from this cyclic voltammetric screening method for a number of charge transport compounds, and compare these results with behavior of the compounds in the electrophotographic environment.

Introduction

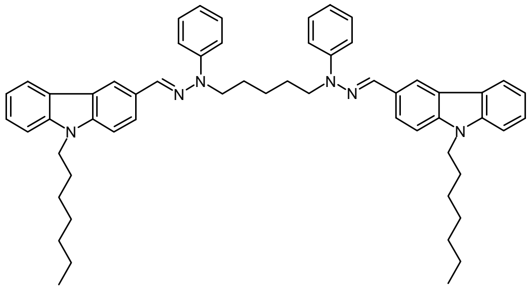
There is interest in developing an inexpensive, rapid, off-line screening test for charge transport materials to be used in electrophotography. The electroanalytical technique of cyclic voltammetry (CV) generates information about charge transport materials that can be correlated to their performance in the photoconductor.

It is difficult to predict exactly how the charge transport material will behave in electrophotographic processes based solely on its electron transfer behavior in the solution phase CV experiment, however many important correlations can be made which makes this a useful screening method. The number of electrons that can be transferred to or from a molecule is readily determined by the number of waves observed in the voltammogram. Even when electron transfer events occur at closely spaced potentials and the waves overlap, it is usually possible to deduce the number of transferred electrons from the magnitude of the total current. The number of electron transfer events possible for a molecule is a function of the number of electroactive sites or functional groups on the molecule, and whether or not there is any interaction among the sites. The potential at which the CV waves are observed is a measure of the thermodynamic ease of electron transfer, and shows good correlation to the ionization potential in a photoconductor film. The redox potentials determined by the CV experiment are affected by several simultaneous and/or consecutive physical and chemical processes. The electronic energies of oxidation determined in the CV experiment are usually higher than those determined spectrophotometrically. However the values correlate fairly well.

The type of transfer occurring, oxidation or reduction, is obvious in the CV data as either an anodic increase in current, or a cathodic increase, respectively. The band gap of the molecule can be approximated from the difference in potential between the first oxidation and the first reduction waves, to derive the highest occupied (HOMO) and lowest unoccupied (LUMO) electronic levels respectively. Any observed change in CV peak potential with increased scan rate is diagnostic for slow electron transfer kinetics, and this information correlates to rate of charge or discharge.

In the CV experiment a triangular potential vs. time waveform is applied between a working and a reference electrode, while the resulting current is measured at a third, auxiliary electrode. The reaction of interest occurs at the working electrode surface. When the current at the auxiliary electrode is plotted versus the applied potential, the i–E curves show hysteresis or peaks, at potentials where electron transfer events have occurred across the solution/ electrode interface. The potential of the peaks identifies individual species undergoing electron transfer, and their currents correspond to the amount of each species present. The electroactive species may be in solution or attached to the electrode surface. These two conditions are readily distinguished by the dependence of the electron transfer current on rate of change of the potential (scan rate).

The cyclic voltammetry experiment provides a wealth of data about the compound's electron transfer characteristics and is useful for making predictions about its performance when incorporated into the charge transport layer of a photoconductor film. We report results of this method on a number of organic charge transport materials. The chemical structures of the molecules studied are shown below. All of these compounds are expected to have good solubility and mobility in the polymer matrix, based on structure. In addition, they possess functional groups that would form charged radical species readily, and are therefore candidates for charge transport agents.



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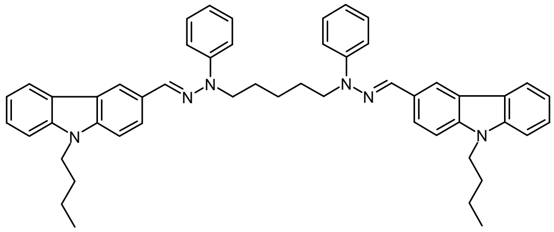

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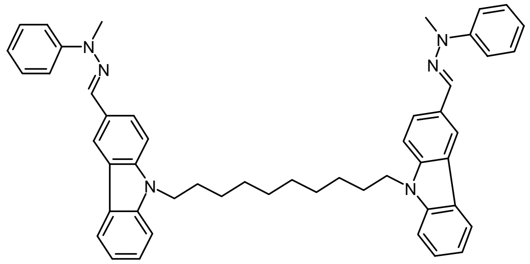

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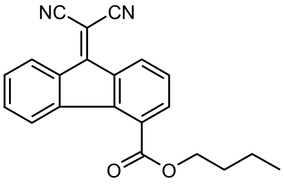

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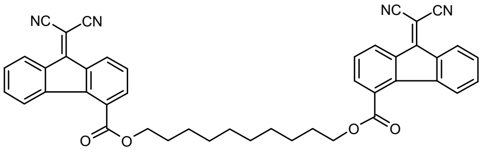

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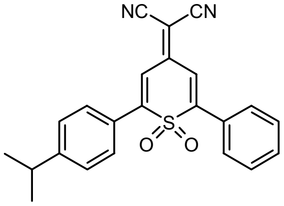

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Experimental

Compounds were used as received without further purification. Electrolyte/solvent solution was prepared to be 0.1 M in tetrabutylammonium tetrafluoroborate in ultra pure, anhydrous dichloromethane. Compounds were dissolved in this electrolyte solution and subjected to analysis by cyclic voltammetry under the following conditions. Working and counter electrodes were platinum flags having total surface areas approximately 1 cm^2 and 2 cm^2, respectively. A silver wire was used as a pseudo reference electrode. Scan range for most samples was from + 0.500 to –2.4 V vs. SRE. No peaks were observed outside of this range that could be attributed to the compounds under study. Scan rates were varied from 10 mv/s to 1000 mv/s, providing three orders of magnitude variation in scan rate. An EG&G Princeton Applied Research model 273A potentiostat and EG&G/PAR M270 and Power Suite / Power CV software were used to control the experiment and acquire the data.

Results and Discussion

Hole Transport Materials:

A typical set of cyclic voltammograms is shown for Compound 1 (Figure 7). The relatively low, positive potential of this first wave shows that oxidation process is thermodynamically favored for Compound 1 and therefore it would function as a hole transport material. The current is observed to increase with the square root of scan rate according to theory for a solution phase species. The peak separation increases with scan rate which is diagnostic for quasi-reversible kinetics, however this separation is not great and the ratio of the cathodic peak current to the anodic peak current is close to 1 at all scan rates, meaning that the process has good reversibility and only little interference from competing side reactions. (See Table 1)

Data for Compound 3 is presented in Figure 8. The oxidation potential is greater meaning electron loss is less favored than for Compound 1. The peak separation is slightly less than for Compound 1, at all scan rates, meaning slightly faster electron transfer kinetics. The peak current ratio is less, meaning the discharge is incomplete for this compound.

Figure 9 shows the CV of an extended scan range for Compound 1. This pattern is typical for this set of compounds in that it shows a second oxidation process occurring at higher anodic potential, and evidence of a third process. The second process is the formation of the di-cation and the third has been identified both from the CV and from visual inspection of the electrode as polymerization of the material on the surface.[1] Anodic oxidation is a common method of preparing organic polymers. When the second electron transfer occurs very close in potential to the first, there is the possibility of generating mixed products when charging the photoconductor. If the photoconductor is charged to an even higher potential, polymerization of the charge transport material could occur resulting in loss of mobility and incomplete discharge.

Figure 10 shows an overlay of voltammograms for the three hole transport compounds examined in this work. The differences in peak potential and current reversibility are clearly seen.

Electron Transport Materials:

CV's for Compound 6 are shown in Figure 11. For this compound, the potential of the first wave is in the cathodic range and the low half-wave potential of about –218 mV vs. SRE shows ease of reduction. Compound 6 would serve well as an electron transport material. Compound 6 also shows the expected scan rate dependence of the current for a solution phase species, a smaller increase in peak separation, and nearly constant peak current ratio of 1, with increased scan rate. This indicates faster electron transfer kinetics than Compound 3, above, and little interference from competing side reactions.

Data for electron transport Compound 4 is given in Figure 12. Several comparisons can be made with Compound 6. The half wave potential for Compound 4 is considerably more cathodic, meaning higher energy required for charging this molecule. Peak separation is greater at all scan rates, meaning the electron transfer kinetics are more sluggish. The peak current ratio is fair, but not as high as for Compound 6, meaning competing side reactions and incomplete discharge.

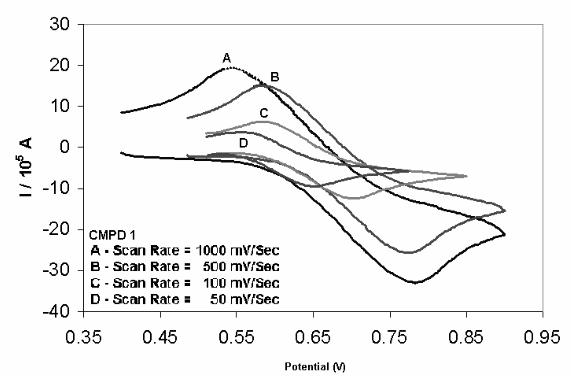

Figure 7. Cyclic voltammogram for low concentration Compound 1 showing the first electron transfer process. Scan rate is varied from 50 to 1000 mv/s.

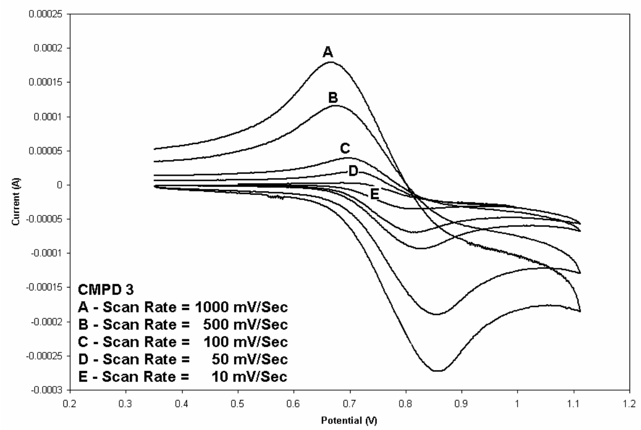

Figure 8. Short range cyclic voltammograms for Compound 3. Scan rate is varied from 10 to 1000 mv/s.

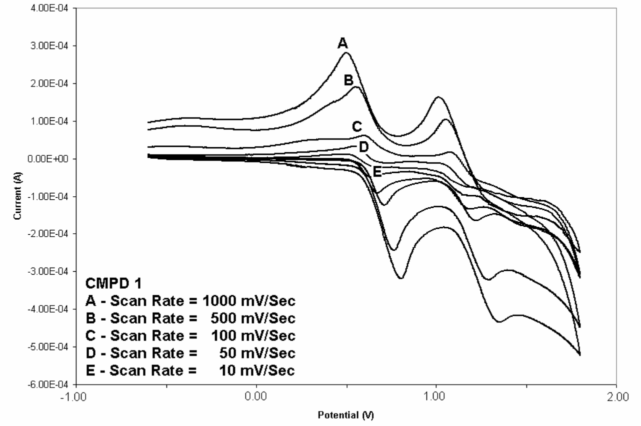

Figure 9. Full potential range voltammogram for Compound 1. Scan rate is varied from 10 to 1000 mv/s.

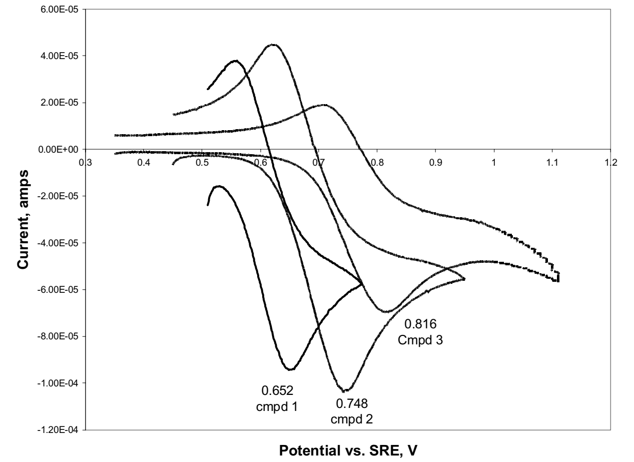

Figure 10. Overlay of first electron transfer process for Compounds 1, 2 and 3. Scan rate is 50 mv/s. Concentrations all approximately 4 mM.

Figure 13 shows the CV of an extended scan range for Compound 4. This pattern is typical for this set of compounds in that it shows a second reduction process occurring at more cathodic potential, and evidence of a third process. The second process is the formation of the di-anion. As for the hole transport materials, when the second electron transfer occurs very close in potential to the first, there is the possibility of generating mixed products when charging the photoconductor. For this electron transport material, the re-oxidation process is even less favored after the second reduction than after the first. This means that even a slight over potential during the charging phase of the photoconductor could result in mixed product with a diminished capacity to discharge.

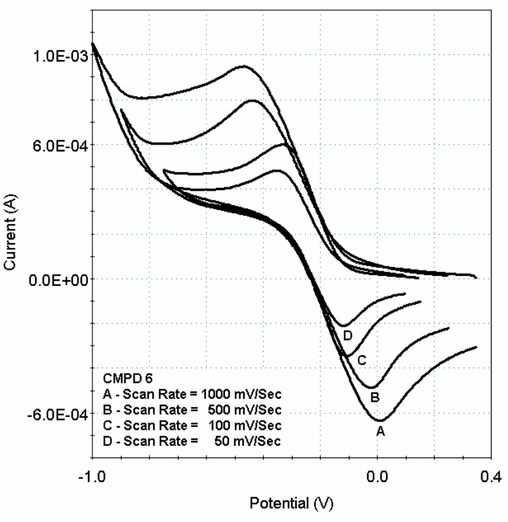

Figure 11. Compound 6, first electron transfer event only. Scan rate is varied from 50 to 1000 mv/s.

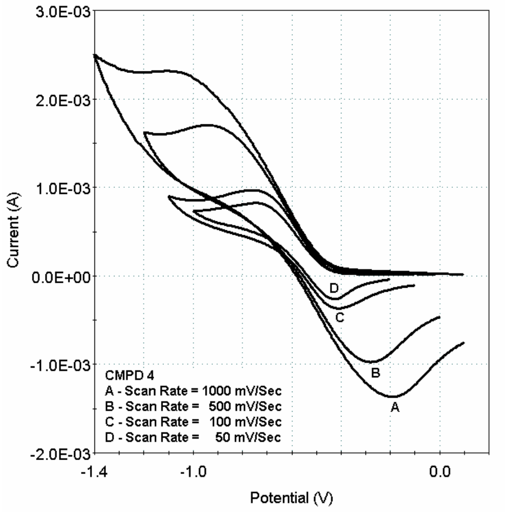

Figure 12. Compound 4, first electron transfer event only. Scan rate is varied from 50 to 1000 mv/s.

Table 1. Summary of Cyclic Voltammetric Data: Compounds are at same concentration, 50 mv/s scan rate

CMPD	Type	1st CV peak potential, mv	ΔEp	Ip ratio
1	hole	674	124	0.951
2	hole	494	126	0.767
3	hole	844	108	0.563
4	e–	–471	225	0.636
5	e–	–490	252	0.136
6	e–	–117	233	1.1

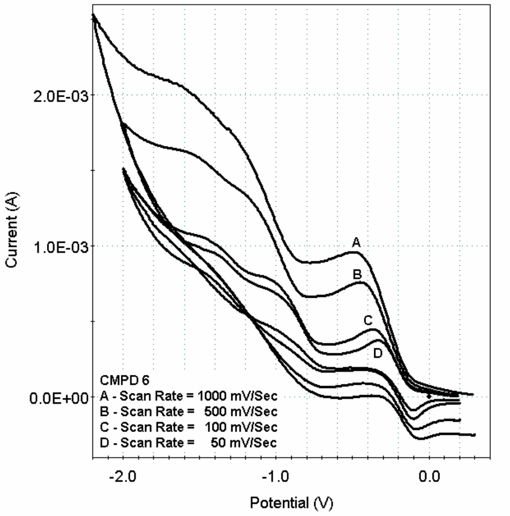

Figure 13. Long range scan for Compound 6, showing multiple electron transfer events. Scan rate is varied from 50 to 1000 mv/s

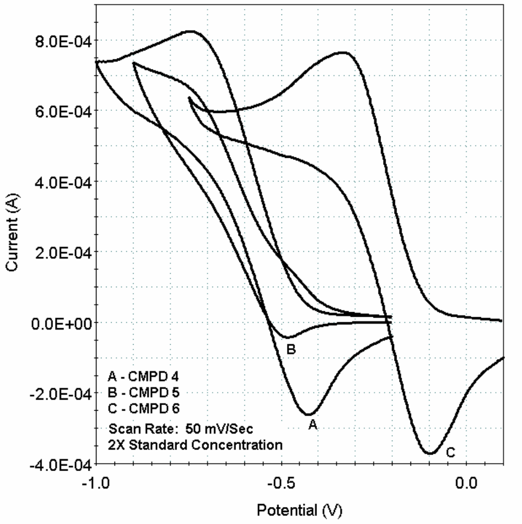

Figure 14. Overlay of Compounds 4 (1.1 mM), 5 (1.2 mM) and 6 (0.6 mM), first electron transfer only. Scan rate is 50 mv/s.

Discussion of Cyclic Voltammetric Results

In this work, we present two sets of materials that show both the strengths and the potential weaknesses of cyclic voltammetry as a predictive tool.

The cyclic voltammetry of Compounds 1, 2 and 3 presents an ambiguous picture. All are clearly capable of function as hole transport materials, but none exhibits a profile that is particularly impressive. Within this particular set, there is no clearly superior hole transporter. Their oxidation potentials are not particularly low. Furthermore, the compound with most reversible electron transfer process based on ΔE_{pp}, (Compound 3) is also the most likely to undergo competing side reactions, based on peak current ratio. The compound with the lowest oxidation potential (Compound 2) also has slower electron transfer kinetics than Compound 3, and poorer reversibility than Compound 1. These facts represent a set of trade-offs in performance, and the three compounds were tested against each other in single layer OPC under the conditions of intended application. All three of the hole transport materials, Compounds 1-3, showed some promise as efficient hole transport materials when used in organic photoconductor configuration,[2] but none was very impressive, as predicted by the cyclic voltammetry.

In contrast to the results for hole transport materials, results for the electron transport materials predict that Compound 6 will be clearly superior in several measurements over Compounds 4 and 5. It has by far the greatest ease of accepting an electron (smallest reduction potential), it has fairly reversible (relatively fast) electron transfer kinetics, and exhibits less tendency to undergo chemical side reactions in the reduced state than either Compound 4 or 5. In this particular set of electron transport materials, the cyclic voltammetric screening test shows it power.

Electron transport materials Compounds 4-5 showed good electrophotographic response in single layer OPC[3] However, Compound 6 clearly outperformed both Compounds 4 and 5 under the same conditions, and this superiority is predicted by the cyclic voltammetry results.

It should be emphasized that the type of charge transport material is not the limitation, but rather the particular members chosen for the test. A set of hole transport materials could have been chosen such that one member of the set would be clearly superior in electrochemical, and thus performance, characteristics. This screening method is equally applicable to hole and electron transport materials.

Conclusion

On the basis of the cyclic voltammetric screening test, Compounds 1, 2, and 3 will serve as hole transport materials because of their relative ease of oxidation. Analysis of the cyclic voltammetric data does not show a clear superiority of one material over another, and the results are somewhat ambiguous. Testing of these materials under printer conditions shows similar ambiguities, and there is no clear favorite. On the other hand, among the electron transport materials, Compound 6 would be clearly favored over Compounds 4 and 5 as an electron transport material. These results are borne out by tests conducted on the charge transport materials under operating conditions.

It is concluded that cyclic voltammetry can be used as a rapid screening test to evaluate candidate molecules. The capacity of a compound to function as either a hole or electron transport material can be clearly determined. Reasonable predictions can be made about charging potential, completeness of discharge, and the kinetics of charging or discharging. In cases where the cyclic voltammetry is ambiguous, more testing under conditions similar to the intended application would be needed. But in the case of three electron transport materials tested in this work, the cyclic voltammetric results were unambiguous and gave the same conclusion as the functional tests of the material.

We expect to continue this work and refine the prediction capabilities of cyclic voltammetry as a rapid screening tool for candidate charge transport materials.

References

1. D. Russell, R. Meyer, N. Jubran, Z. Tokarski, R. Moudry, K. Law, “Electrochemistry of some novel hole transport materials”, J. Electroanal. Chem., 567 (2004) 19-27.
2. U.S. patent Nos. 6,140,004 and 6,670,085
3. U.S. Patent Pending

Biography

Dr. Russell is a professor at Boise State University and holds joint appointment to both the Chemistry and Materials Science departments. She earned a Ph.D. in Chemistry from the University of Arizona in 1985. She worked at Hewlett-Packard Company for several years in non-impact printing technologies, color science, and print quality before joining Boise State. Her current research interests include electrochemistry, electrochemical sensors, and electrokinetic methods of materials characterization. drussell@boisestate.edu