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Redox Potential Measurements of Spectral Sensitizing Dyes by Means of Fast Scan Cyclic Voltammetry

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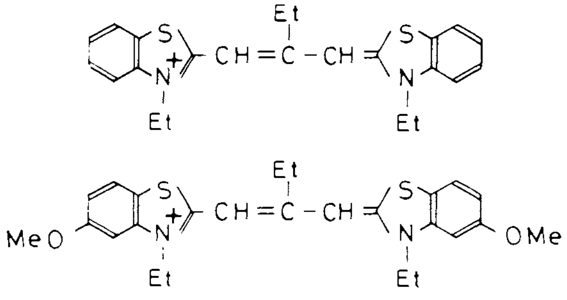
Fast scan cyclic voltammetry dramatically reduced the effect of consecutive chemical reaction involved in electrooxidation or reduction process of cyanine dyes. This electrochemical measurement has enabled to obtain more correct redox potentials of the dyes directly from cyclic voltammograms allowing more exact electrochemical characterization of spectral sensitizing dyes.

For the electrochemical characterization of spectral sensitizing dyes, which are used for spectral sensitization of silver halide, their formal potentials are commonly used.[1,2] However, products generated in electrooxidation or reduction process are in most cases unstable and undergo the successive chemical reactions such as dimerization reaction at relatively short time scale. Due to this chemical follow-up reaction, voltammograms obtained with conventional dc polarography or cyclic voltammetry (CV) are mostly distorted and measurements of the redox potential are difficult. Our newly developed fast scan cyclic voltammetry (FSCV) has enabled to reduce the effect of the consecutive chemical or electrochemical reaction involved in electrode processes. Scan rate faster than 1 kV/s reduced the measurement time scale shorter than the time scale of the chemical reactions and gave voltammograms with well defined current peaks during backward potential scan. This allowed us to estimate more accurate formal redox potentials of the dyes directly from cyclic voltammograms.

The system configuration of the FSCV has already been reported.[3] In the previous study on fabrication of ultra micro disk electrode (UMDE), the rapid response UMDE with low impedance was developed.[4] The UMDE was also designed to decrease the charging current, which becomes extremely large at fast scan rate. With this FSCV system using the UMDE, scan rate up to 1 MV/s is available and the response time of the system is less than 1 μs. Ohmic potential drop was less than 10 mV even at the scan rate of 30 kV/s with the platinum UMDE of 10 μm diameter.

The FSCV measurements were carried out with Pt UMDE of 10 μm diameter. A platinum wire of 0.5 mm diameter was used for a counter electrode. The double-junctioned assembly consisting of a Pt/(I_3^-, I^-) reference electrode, which was recommended by Coetzee et al.,[5] was used. (Potentials are shown versus this electrode.) Potential of this reference electrode was 120 mV versus saturated calomel electrode (SCE).

Spectral sensitizing dyes (3,3'-diethyl-9-ethyl-thiacarbocyanine, described as **Dye 1**, and 3,3'-diethyl-9-ethyl-5,5'-dimethoxy-thiacarbocyanine, **Dye 2**, whose structures are shown in Fig. 1) were kindly supplied in the forms of p-toluensulfonic acid (PTS) salts from Mr. Katsuhisa Ozeki of Fuji Photo Film Co. Ltd.



Dye 1

Dye 2

Fig. 1. Structures of Dye **1** and Dye **2**.

Tetraethylammonium hexafluorophosphate ($TEAPF_6$) was synthesized and acetonitrile (AN) was redistilled according to as reported.[3)] The sample solution containing 0.5 M (1 M =1 mol dm^{-3}) $TEAPF_6$ and 5 mM each dye in AN was deoxygenated by nitrogen gas before measurements. Voltammograms in Fig. 2 and the potential values in Table 1 were obtained on the average of ten (conventional CV with the scan rate of 0.1 V/s) and fifty (FSCV with the scan rates of 1 - 10 kV/s) successive measurements.

Figure 2 shows cyclic voltammograms obtained by both conventional CV and FSCV. Voltammograms obtained by conventional CV were seriously distorted by the consecutive chemical reaction and the current peaks by the backward potential scan were difficult to be identified (or couldn't be observed). On the other hand, the well defined current peaks by the backward potential scan were observed in voltammograms at the scan rate faster than 1 kV/s. Appearance of the well defined backward scan current peaks shows that the effect of consecutive chemical reaction could be greatly removed. Remarkable shift of forward scan peak potential (E_{pf}) (to positive in case of oxidation and negative in case of reduction) between two scan rates of 0.1 V/s and 1 kV/s also confirms this fact. Appearance of backward scan peak allows practical estimation of the formal redox potential, that is, the formal redox potential is estimated as the mid point potential of the two peak potentials corresponding to forward scan peak potential (E_{pf}) and backward scan peak potential (E_{pb}). Estimated formal redox potentials (E_O^0 for oxidation and E_R^0 for reduction of dyes) at each scan rate are listed in Table 1.

Our estimations of formal redox potentials were carried out even though the ratios of forward scan peak current (i_{pf}) and backward scan peak current (i_{pb}) were still less than unity and the peak separations(E_{sep}) are somehow larger than expected in the reversible case. However, it is of great importance that the estimation of redox potentials was based upon less distorted two peak potentials (E_{pf} and E_{pb}). Otherwise in case of conventional cyclic voltammograms, estimation of the redox potentials must be based upon only seriously distorted E_{pf}, which requires compensation of the consecutive reaction in some way or other. Considering remarkably small deviations of the estimated formal redox potentials according to the scan rate, those values were not distorted by consecutive chemical reaction anymore. Although quasi-reversibility of the voltammograms caused slight positive shift (in case of oxidation) or negative shift (reduction) of those redox potentials according to the scan rate, the deviations were only within 10 mV, which were small enough for the formal redox potential measurements.

In the field of photochemical engineering where precise characterization of numerous kinds of dyes are required, FSCV can be greatly appreciated as the feasible and reliable measurement method of dye redox potentials. Reduced measurement time of this FSCV is also appreciated because, given the same time, much more series of accumulation and averaging of the voltammograms are possible.

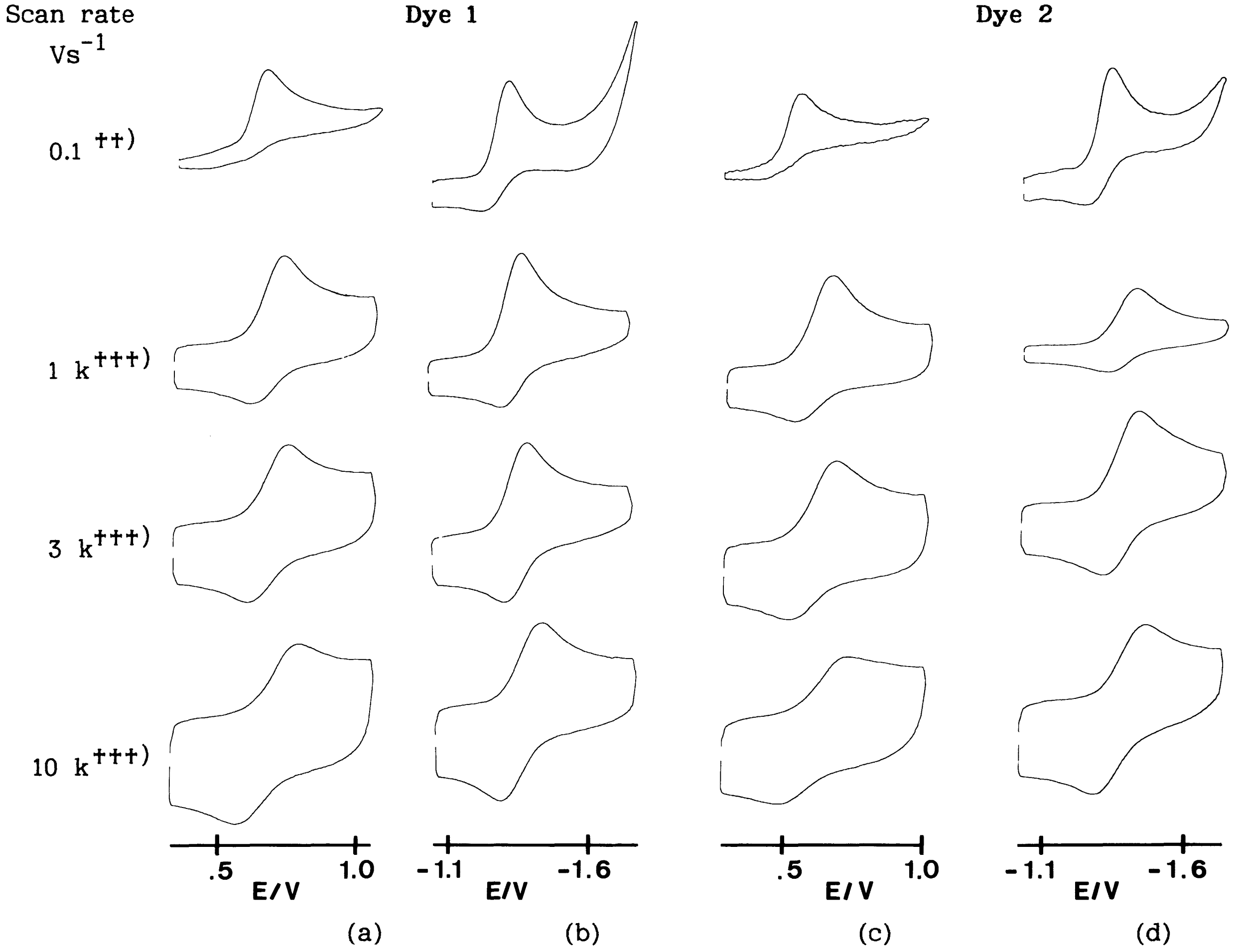


Fig. 2. Cyclic voltammograms†) of Dyes 1 and 2. (a) Oxidation and (b) reduction processes of Dye 1, (c) oxidation and (d) reduction processes of Dye 2.

†) Potentials are referred to versus Pt/(I_3^-, I^-).

††) Conventional CV (average of ten successive measurements).

†††) FSCV (average of fifty successive measurements).

In the case of these dyes, the use of faster scan rate than 10 kV/s was not effective, but they gave only distorted voltammograms with less defined peaks and E_{sep} values larger than 200 mV. It seems to be due to relatively slow electron transfer rates of those dyes, which does not mean the limitation of the applicability of FSCV to redox potential measurements of spectral sensitizing dyes. For the measurements of the dyes involving more rapid consecutive chemical reaction, the rate of the consecutive reaction can be reduced by choosing the proper solvent. Indeed, according to our preliminary experiment for the reduction of cyanine dyes in DMF solution, slowdown of the chemical follow-up reaction was observed, giving more defined peak current during backward potential scan. In addition, feasibility of theoretical treatment on cyclic voltammogram opens up our way. Combined with digital simulation,3) this FSCV will allow the redox potential measurements of dyes involving more rapid consecutive reaction. This will also enable the theoretical consideration on the propriety of our estimation of the dye formal redox potentials. Such studies are now in progress.

Table 1. Peak potentialsa) and formal redox potentialsa) of the dyes at each scan rate

Dye	Scan rate	Oxdation					Reduction				
	Vs^{-1}	E_{pf}	E_{pb}	E_O^0	E_{sep}	i_{pf}/i_{pb}	E_{pf}	E_{pb}	E_R^0	E_{sep}	i_{pf}/i_{pb}
Dye 1	0.1	610	-	-	-	-	-1330	-	-	-	-
	1 k	720	605	660	115	.46	-1375	-1295	-1335	80	.36
	3 k	735	605	670	130	.45	-1385	-1290	-1340	95	.51
	10 k	780	570	675	210	.58	-1420	-1270	-1345	150	.72
Dye 2	0.1	560	-	-	-	-	-1280	-	-	-	-
	1 k	655	535	595	120	.31	-1395	-1300	-1350	95	.31
	3 k	675	525	600	150	.37	-1410	-1300	-1355	110	.45
	10 k	720	490	605	230	.39	-1450	-1270	-1360	180	.64

a) Potentials are shown in mV vs. Pt/(I_3^-, I^-) as mean values of ten (0.1 V/s) and fifty (1, 3, and 10 kV/s) scans.

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