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Solid state electrochemical reaction in photocells made using conducting polyaniline and sensitized with methylene blue

Abstract The effect of small concentration of methylene blue (MB) on photocurrents was studied in solid state photoelectrochemical cells fabricated using conducting polyaniline (PANI) coated electrodes sandwiched with a solid polymer electrolyte, viz. poly(vinyl alcohol) (PVA) with phosphoric acid. These exhibit good photoresponse to visible light (maximum photosensitivity factor of the order of 10). The current-voltage (*I-V*) characteristics in such cells reveal that the charge transport is ohmic. Also, an electrochemical reaction (motion of Cl^- from SPE + MB to PANI) is observed at 1.2–1.3 V, which gives rise to a sudden increase of current at this particular voltage. The presence of illumination enhances this electrochemical reaction. The combined effect, i.e. ohmic charge transport and an electrochemical reaction, is observed in the *I-V* characteristics. Along with the dye concentration, the photosensitivity is observed to be field/voltage dependent. The sensitization effects are due to lowering of the potential barrier formed at the PANI/ SPE + MB interface under illumination.

Keywords Dye sensitization · Solid state electrochemical cells · Solid polymer electrolyte · Conducting polymers · Polyaniline

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Introduction

Conducting polymers are finding increasing numbers of applications in various electronic devices such as electrochromic displays (ECD), light emitting diodes (LED), chemical sensors, etc. [1, 2, 3, 4, 5, 6, 7, 8, 9]. Like photovoltaic devices, the devices which are useful for photoenergy conversion are photoelectrochemical (PEC) cells, which showed promising results but could not be used for practical applications owing to some drawbacks [10, 11]. One of the major drawbacks for such cells has been the liquid electrolyte component, which makes it difficult to fabricate in large areas. Some attempts have been made in the past for replacement of the liquid electrolyte with a solid polymer electrolyte [12, 13]. However, these authors have used conventional inorganic semiconductors such as TiO_2, ZnO, etc., for the active photoelectrode, which, again, does not ease the method of processing. Another drawback of these cells has been the very low photocurrents obtained owing to the cell resistance and/or low photosensitivity of the material. The photosensitivity of such materials can be enhanced (and/or extended into the visible region) by the use of dyes and pigments. We made attempts in the past to fabricate PEC cells using simultaneously conducting polymers and solid polymer electrolytes [14, 15, 16]. We report here our studies on such photocells made using conducting polyaniline (PANI) and sensitized with methylene blue (MB) dye. Studies were also done in order to understand the charge transport mechanism in such cells. Charge transport is mainly ohmic in nature. A solid state electrochemical reaction is also observed to occur in the photocells under the present investigations.

Experimental

The photocells were fabricated by the following method. First, thin gold films were deposited on clean microscopic grade glass substrates. Conducting PANI films were deposited on these by standard potentiostatic technique [17] using a single-compartment

electrolytic cell having a platinum counter electrode, a saturated calomel reference electrode (SCE) and aqueous hydrochloric acid (0.5 M) in which the aniline monomer (0.1 M) was thoroughly mixed. Electrochemical polymerization was carried out potentiostatically at 0.7 V vs. SCE for 150 s. The PANI films obtained were washed, dried and used for further study. PANI films were also deposited on the indium-tin-oxide (ITO) electrode (20 Ω/sq) at the same experimental conditions. Knowing the optical density of these films from the UV-Vis spectra, the thickness of the film is estimated. Throughout the study, the PANI film thickness is kept practically constant (approximately 500 nm). The PANI films are observed to be of fairly uniform thickness. These were subsequently dip-coated with poly(vinyl alcohol) (PVA, MW 10^4, Loba Chemie) films containing phosphoric acid (1:1) from aqueous solution (1 wt%), which also contained MB dye (Loba Chemie) in the concentration range 0–6 mM/monomer unit. These were then dried at room temperature and pressed against a transparent conducting (20 Ω/sq) ITO-coated glass so as to form the sandwich cell configuration as shown in Fig. 1. The active area of the electrode is 2×2 cm^2. The current-voltage (I-V) characteristics of these cells were studied in the dark and under white light illumination (5.0 mW/cm^2, tungsten lamp source) in the same manner as described elsewhere [14, 15, 16, 18].

Results and discussion

The I-V characteristics in the dark (D) and under illumination (L) for these photocells are as shown in Fig. 2. The curves (A)–(D) correspond to MB dye concentrations of 2.7, 3.3, 4.1 and 5.3 mM/monomer, respectively. It is interesting to observe that the I-V characteristics in the dark exhibit a rectifying nature, i.e. the current in one direction (Au +ve, 1st quadrant) is much higher than in the opposite direction (Au –ve, 3rd quadrant). The variation of the photosensitivity factor ($S = I_l/I_d$, where I_l is the photocurrent and I_d is the dark current) with respect to the MB concentration for these cells is as shown in Fig. 3. It is quite evident that there is a certain MB concentration (4.1 mM/monomer) at which the photosensitivity is observed to be maximum (of the order of 10). The concentration of the MB dye corresponding to the maximum photosensitivity factor is said to be the "critical concentration". Initially, with increase in MB concentration and below the critical concentration, photosensitivity increases because of the increase in the number of the sensitizing centres. After the critical concentration of the dye, the photosensitivity decreases. This must be due to the heavy trapping followed by the recombination of the photogenerated charge carriers within the bulk. Also, at very high concentration of the dye, light (photons) is being absorbed only at the surface and is unable to penetrate to the junction. It is worthwhile to mention here that another possibility, the increase of crystallinity through increased MB concentration leading to easier exciton diffusion to the quenching site, is ruled out because MB when incorporated in a SPE (PVA + H$_3$PO$_4$) matrix forms a complex with the polymer by a hydrogen bonding interaction between the OH group of the polymer (PVA) and the nitrogen of MB. Also, study of MB-incorporated SPE films on glass substrates deposited by the dip coating method by XRD, UV-Vis and optical microscopy reveals that MB is not present in an aggregated, crystalline form in SPE [18, 19]. This is also reflected in the I-V characteristics (presented in Fig. 2), where it can be observed that the dark current increases with increase in the MB dye concentration, whereas the photocurrent, which was low at low MB concentrations, increases with it and then again decreases with a further increase of dye concentration. Thus, the variation of the photosensitivity factor with the MB dye concentration goes through a maximum. From the I-V characteristic curves presented in Fig. 2 it can be observed that the photosensitivity is field/voltage dependent.

Figure 4 shows the I-V characteristics plotted on a log-log scale and it is evident from these curves that the relation $I \propto V^n$ is indeed followed with $n \approx 1$, indicating ohmic charge transport. However, the slope of the graph changes considerably with the increase in the MB content as well as the presence of illumination. These curves are quite interesting and look to be the superimposition of ohmic charge transport and an electrochemical reaction, as there is a sudden rise of the current values at 1.2–1.3 V which is observed in all the samples and at the same voltage. It should be noted here that MB incorporated in PVA + H$_3$PO$_4$ (SPE) contains Cl$^-$ from MB. On application of the positive potential (and particularly at about 1.2–1.3 V) to PANI, Cl$^-$ must be moving from the SPE/MB to PANI with a resultant increase in the doping level of PANI. The conductivity of the PANI will increase as more and more Cl$^-$ enter. As the concentration of the MB dye increases, it has been observed that the current at this particular voltage increases more and more, which is in good agreement with the proposed mechanism. This electrochemical reaction must be occurring at 1.2–1.3 V, yielding a rise in the current

Fig. 1 Schematic diagram of the solid state photocells using conducting polyaniline (Au/PANI/SPE + MB/ITO)
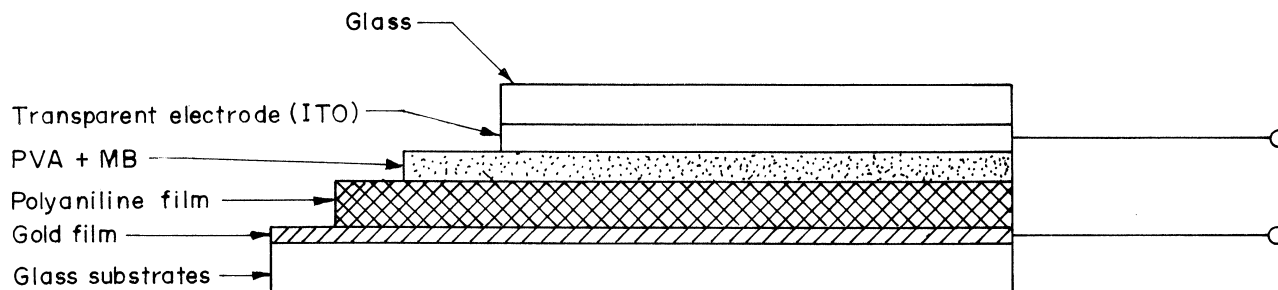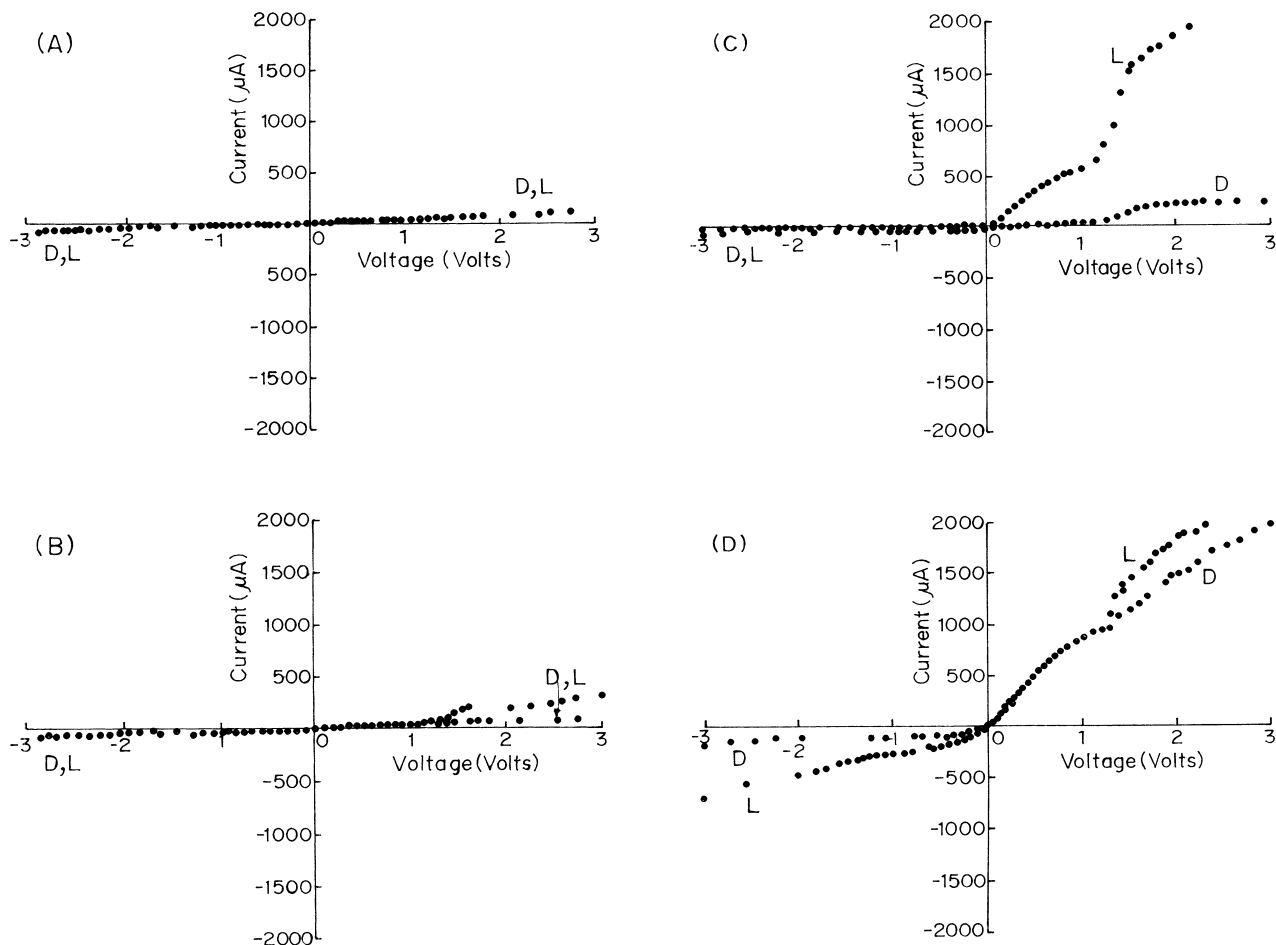
Fig. 2 Current-voltage (*I-V*) characteristics in the dark (*D*) and under illumination (*L*) for the photocell Au/PANI/SPE + MB/ITO containing different concentrations of MB: (**A**) 2.7, (**B**) 3.3, (**C**) 4.1 and (**D**) 5.3 mM/monomer, respectively
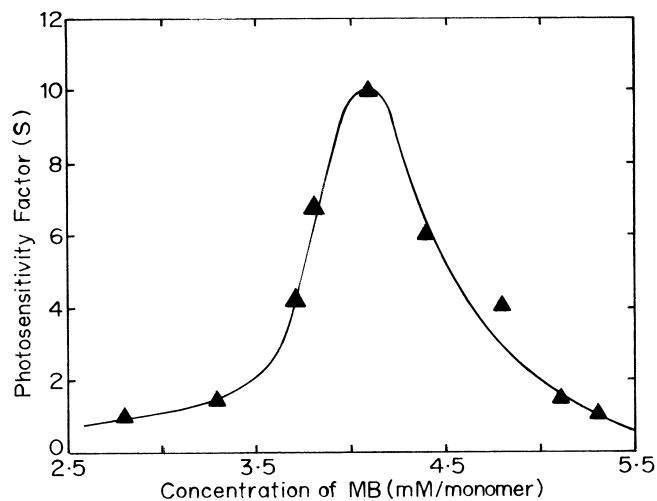

Fig. 3 Photosensitivity factor (*S*) as a function of the concentration of MB for the photocell Au/PANI/SPE + MB/ITO

value at this particular voltage. The presence of illumination is observed to enhance this electrochemical reaction. It is worthwhile to mention here that the conductivity of PANI, in particular, is very much dependent on its doping level and the degree of protonation.

The mechanism of the sensitization process can be understood in terms of energy band levels for the materials used in forming the photocells. Figure 5 depicts the different energy levels for the materials used for forming the photocell Au/PANI/SPE + MB/ ITO. The energy levels for PANI (4.4 eV LUMO and 5.9 eV HOMO) are those which have been reported in the literature [20], while those for MB in PVA are derived from the UV-Vis spectra recorded and using the reported energy levels [21]. Also, it should be remembered that MB is a p-type dye [21]. It must be noted that the PVA-containing phosphoric acid is a good proton conductor, while doped PANI is a p-type material. The work function of Au is at 5.22 eV. Considering the Au/PANI interface, it can be seen that electrons feel more barrier (0.82 eV) than that of the holes (0.68 eV). Thus one can say that Au makes an ohmic contact for holes with the PANI, as compared to the electrons. ITO makes a blocking contact (for both electrons and holes, more for electrons) with PVA/MB. Thus, when Au is positive, the hole transport via PANI and the proton transport through PVA
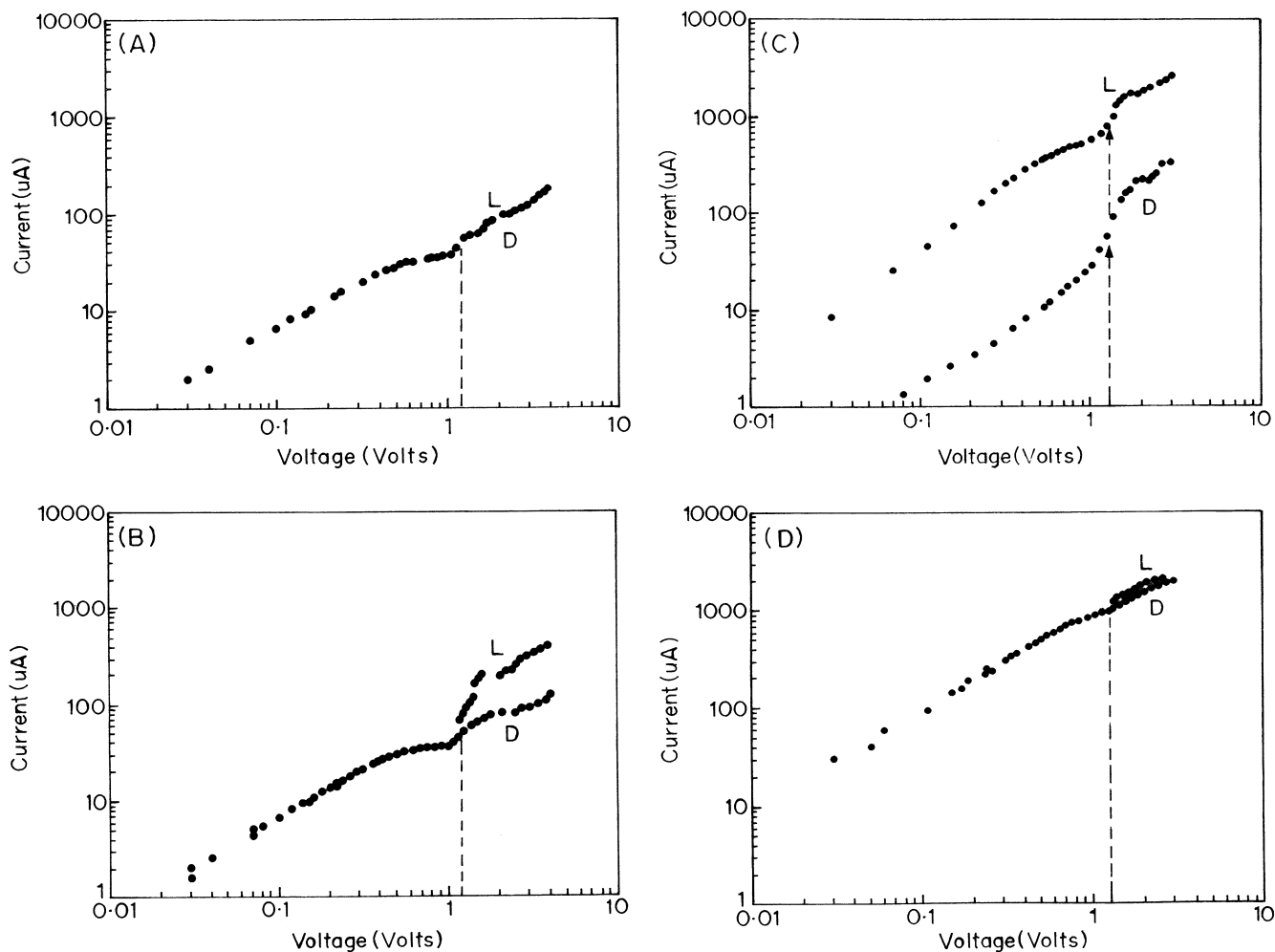
Fig. 4A–D Log-log plot of the *I-V* curves showing ohmic charge transport. Curves **A–D** correspond to the MB concentrations of 2.7, 3.3, 4.1 and 5.3 mM/monomer, respectively

are facilitated, giving high forward current, although some barrier is expected at the Au/PANI interface. On the other hand, when Au is having negative polarity, the current would be less since electrons are minority carriers (in both PANI and PVA + MB, since MB is a p-type dye) and a barrier is expected at the Au/PANI and PANI/PVA + MB interfaces. This gives rise to the rectifying type *I-V* characteristics as noted in the present case. On the other hand, when the photocell is under illumination, MB dye absorbs light and fills the higher electronic levels with photoexcited charge carriers. This facilitates their transport across the potential barriers and the required effect is observed. It should also be remembered that there are several other energy levels present, owing to the inherent amorphous nature of the polymer, and hence some of these can act as carrier trapping centres for one type of charge carrier, leaving the other type of charge carrier free to move. In this manner, photosensitivity is obtained by lowering the potential barrier at the polymer/dye interface.
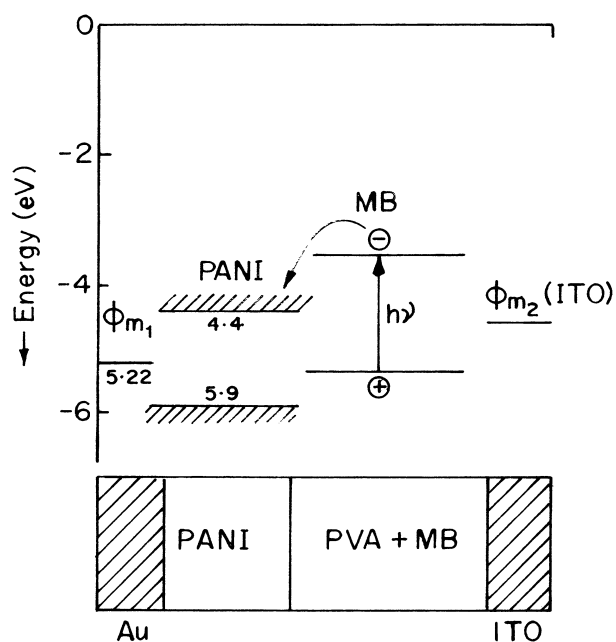

Fig. 5 Energy level diagram for the photocell having a Au/PANI/ SPE + MB/ITO-type sandwich structure

Conclusions

It is observed that MB sensitizes conducting PANI in solid state electrochemical cell configurations. A maximum photosensitivity factor (S_{max}) of the order of 10 has been observed. There is a "critical concentration" of the dye at which maximum photosensitivity has been observed (in the present case, 4.1 mM/monomer). As we go away from this concentration, on both the sides, the photosensitivity decreases. Charge transport is observed to be ohmic in nature. An electrochemical reaction (movement of Cl^- from PVA/MB to PANI) is also observed to occur at 1.2–1.3 V, giving rise to additional doping of the polymer and resulting in an increase of the current values at this particular voltage. The observed I-V characteristics are the superposition of the ohmic charge transport and the electrochemical reaction, the role of the latter being only to increase the current at the particular voltage mentioned above. The photosensitivity factor (S), along with the dye concentration, is also observed to depend on the voltage/field.

References

1. Chilton JA, Goosey M (1995) Special polymers for electronics and optoelectronics. Chapman and Hall, London
2. Bredas JL, Salaneck WR, Wegner G (1996) Organic materials for electronics. Elsevier, Amsterdam
3. Scrosati B (1995) Applications of electroactive polymers. Chapman and Hall, London
4. Braun D, Heeger AJ (1982) Appl Phys Lett 58:1982
5. Gustafson G, Cao Y, Treacy GM, Klavetter F, Colarini N, Heeger AJ (1992) Nature 357:477
6. Somani PR, Radhakrishnan S (1998) Chem Phys Lett 292:218
7. Somani PR, Mandale AB, Radhakrishnan S (2000) Acta Mater 48:2859
8. Somani PR, Viswanath AK, Aiyer RC, Radhakrishnan S (2001) Org Electron 2:83
9. Somani PR, Viswanath AK, Aiyer RC, Radhakrishnan S (2001) Sens Actuators B 80:141
10. Kaneko K, Whorle D (1988) Adv Polym Sci 84:143
11. Bockris JM (1987) In: Alcacer L (ed) Conducting polymers – special applications. Reidel, Dordrecht, chap 1
12. Skotheim TA, Inganas O (1985) J Electrochem Soc 132:2116
13. Ratner MA, Shriver DF (1988) Chem Rev 88:109
14. Radhakrishnan S, Somani PR (1998) Mater Lett 37:192
15. Somani PR, Amalnerkar DP, Radhakrishnan S (2000) Synth Met 110:181
16. Somani PR, Radhakrishnan S (2001) Mater Chem Phys 70:150
17. Diaz AF, Rubinson JF, Mark HB (1988) Adv Polym Sci 84:114
18. Somani PR (2001) Optoelectronic properties of dye sensitized conducting polypyrrole films, PhD thesis, Pune University, Pune, India
19. Somani PR, Marimuthu R, Viswanath AK, Radhakrishnan S (2002) Polym Degrad Stab (in press)
20. Scrosati B (1995) Applications of electroactive polymers. Chapman and Hall, London
21. Seanor DA (1982) Electrical properties of polymers. Academic Press, London, p 134