

Rectification and Photovoltaic Properties of a Schottky Barrier Cell using Electrochemically-doped Poly(*N*-vinylcarbazole)

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An electrochemically-doped poly(*N*-vinylcarbazole) film sandwiched between aluminium and gold electrodes shows rectification and photovoltaic effects.

Recently there has been growing interest in the fabrication of devices using organic electrical conductors. Secondary batteries and solar cells using all π -conjugated polymers such as polyacetylene¹⁻⁴ and polythiophene^{5,6} have been reported. We have reported that insulating, non-conjugated pendant polymers, *e.g.*, poly(*N*-vinylcarbazole) (PVCz), which is a photoconductive polymer, and poly(vinylferrocene), are transformed into electrically conducting polymers by electrochemical doping^{7,8} and that the electrochemically-doped PVCz functions as a positive electrode material for a rechargeable lithium battery.⁹

We report here rectification and photovoltaic properties of a Schottky barrier cell using electrochemically-doped PVCz. Photovoltaic properties of organic photoconductive compounds have been reported: they include chlorophyll,¹⁰ a PVCz-2,4,7-trinitrofluorenone charge-transfer complex,¹¹ metal and metal-free phthalocyanines,^{12,13} squaric acid derivatives,¹⁴ merocyanine dyes,¹⁵ and poly(*p*-phenylene sulphide).¹⁶ The energy conversion efficiencies for organic photovoltaic cells are much lower compared to those for inorganic solar cells. Generally organic compounds have high electrical resistivity; therefore, decreasing the bulk resistivity by doping is one approach for improving the power conversion efficiency of organic photovoltaic cells.

The electrochemical doping of PVCz was carried out for thin films cast on a Nesa glass electrode by controlled-potential anodic oxidation at 1.0 V vs. Ag/Ag⁺ 0.01 mol dm⁻³ reference electrode with a platinum plate counter electrode in the presence of Buⁿ₄NClO₄ as supporting electrolyte in

acetonitrile. After electrolysis for an appropriate time, the green-coloured, electrochemically-doped PVCz film was peeled off the Nesa glass electrode, washed with acetonitrile, and dried *in vacuo*. The electrochemically-doped PVCz is a partially oxidized cation radical salt with ClO₄⁻ as a counter anion. Its structure is partially cross-linked at the 3- or the 6-position of the carbazole ring owing to the coupling reaction of the carbazole cation radical.^{7,9} The electrochemically-doped PVCz film with a thickness of *ca.* 10 μ m was sandwiched between semi-transparent aluminium and gold metals, which were vacuum-deposited onto the film to form the front and back electrodes, respectively.

Figure 1 shows a dark current-voltage (*J*-*V*) curve of the Al/electrochemically-doped PVCz (extent of doping: 14.7%)/Au cell when a positive voltage is applied to the Au electrode with respect to the Al electrode. The cell clearly shows rectification behaviour with a rectification ratio of *ca.* 110 at ± 5.0 V: this indicates that a Schottky barrier is formed at the interface between aluminium and the electrochemically-doped PVCz film which acts as a p-type semiconductor. No such behaviour was observed for a cell using a PVCz film (*ca.* 10 μ m thick) without electrochemical doping. Figure 2 shows the *J*-*V* characteristics of the cell under illumination through the Al electrode (transmittance 4.5%) with 366 nm monochromatic light of varying intensities. As seen in Figure 2, an open circuit voltage *V*_{oc} of 1.01 V, a short circuit current *I*_{sc} of 182

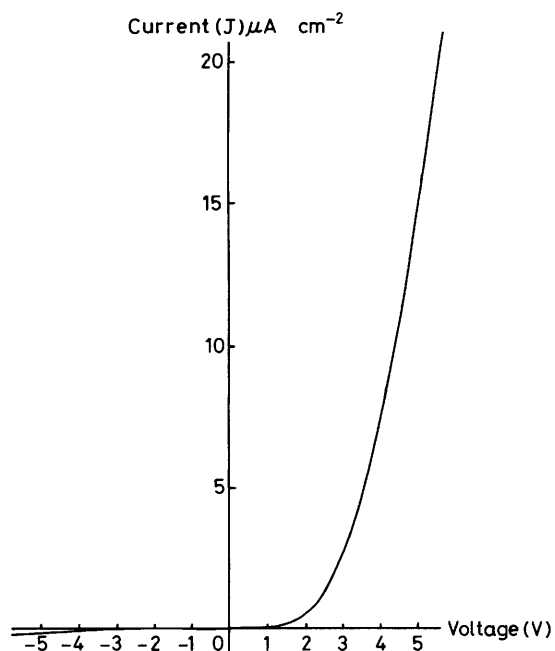


Figure 1. *J*-*V* Curve of the Al/electrochemically-doped PVCz/Au cell in the dark.

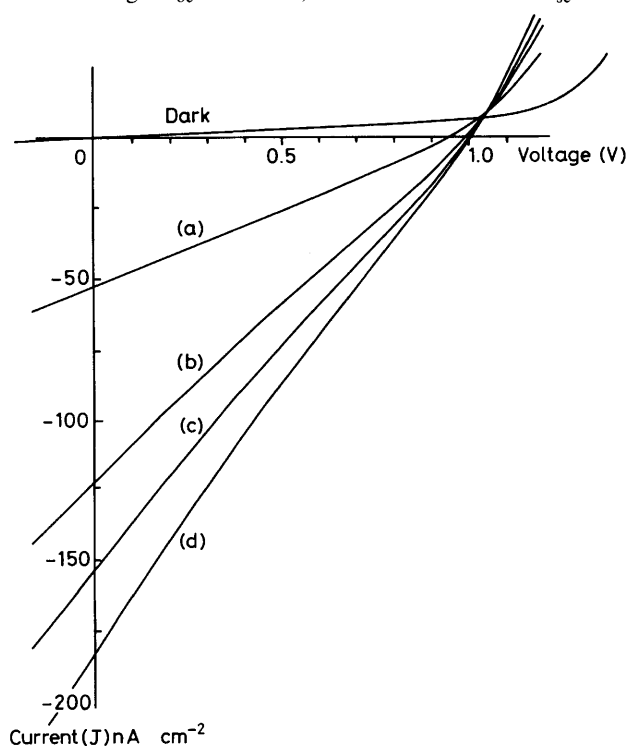


Figure 2. *J*-*V* Curves of the Al/electrochemically-doped PVCz/Au cell under illumination with 366 nm light of varying intensities. Incident photon power (mW cm^{-2}): (a) 1.06, (b) 3.31, (c) 4.51, (d) 6.63.

nA cm⁻², and a fill factor of 0.237 were obtained for the cell when illuminated at 6.63 mW cm⁻². The power conversion efficiencies were in the range from 1.5×10^{-2} to 2.8×10^{-2} % for the transmitted monochromatic light with incident photon power of 6.63 to 1.08 mW cm⁻².

Although the spectral response of PVCz is not in the visible region, it is expected that this method of decreasing the bulk resistivity by electrochemical doping is capable of being extended to other organic photoconductive compounds with the spectral response in the visible region for use in the fabrication of organic solar cells.

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