Photochemical Experiments with Ag/AgCl Electrodes**

Robert Beer, Gion Calzaferri*, and Werner Spahni

Abstract: Quantitative experiments on the photo-induced chlorine evolution in aqueous dispersions of silver zeolites containing chloride ions have shown that the system is capable of spectral sensitization, an effect we call self-sensitization. There was an argument that the photoproduction of chlorine with visible light is only possible immediately after exposing the system to UV-photons. We now deliver experimental results which unequivocally prove that this is wrong. The large driving force of the back reaction $Ag + \frac{1}{2} Cl_2 \rightarrow AgCl$ of $E^0 = 1.14$ V must be considered to approve the photoproduction of chlorine with visible light. Despite of the high electrochemical potential, the recombination reaction is kinetically blocked. Based on these observations we have succeeded to construct a photogalvanic $\{Ag/AgCl\|Cl^\ominus/Cl_2\}$ cell with a theoretical open-circuit potential of 1.14 V. Experimental open-circuit potentials of 1.05 V are regularly obtained and the power voltage curves exhibit a maximum around 730 mV. Encouraging experiments carried out with sunlight show the interesting performance of the system and the advantage of the short-time storage capacity.

$Ag^\oplus$-exchanged zeolites are sensitive to light. In aqueous dispersions under irradiation, they evolve oxygen from water while $Ag^\oplus$ is reduced to Ag. Quantitative experiments have shown that the system is photoactive in the whole visible spectrum due to an effect we call self-sensitization[1]. In presence of $Cl^\ominus$ at low pH, the system evolves Cl_2 with high quantum yield when irradiated in the region of $\lambda = 370$ nm[2] and it reveals a similar type of self-sensitization as the photo-oxygen evolution[3]. A precipitation of AgCl evolves chlorine too under the same conditions but with much lower efficiency.
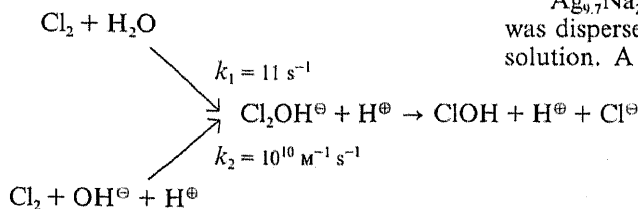
In his investigations to the question «How does light act on pure silver chloride, silver bromide, and silver iodide?» *Hermann Vogel*[4] points out that in the year 1777 – 87 years before the photographic process was invented – *Scheele* was the first to study the effect of sunlight on silver chloride. *Scheele* observed that sunlight blackens silver chloride. After treating the irradiated samples with ammonia, he observed that metallic silver remained and concluded that sunlight decomposes silver chloride into silver and chlorine. *Vogel* himself concluded from indirect observations that silver chloride, silver bromide, and silver iodide decompose into silver and the halogens under exposure to sunlight. 210 years after the discovery of *Scheele*, why do we still look into the reaction $AgCl \xrightarrow{h\nu} Ag + \frac{1}{2} Cl_2$?

Chlorine is thermodynamically stable only at low pH and reacts with water to chloride and hypochlorous acid at pH > 4 according to:

$$HOCl + Cl^\ominus + H_3O^\oplus; \quad pK\,(25\,°C) = 3.47$$

The kinetics of this reaction has been studied, with the finding that the major pathway for the hydrolysis involves attack of H_2O and/or $OH^\ominus$ at the Cl_2 molecule to displace $Cl^\ominus$ and form HOCl. For the pathway involving attack of H_2O upon the halogen, the rate-controlling step is the formation of the intermediate $Cl_2OH^\ominus$; whereas for attack on Cl_2 by $OH^\ominus$, the rate-controlling step appears to be the dissociation of $Cl^\ominus$ from $Cl_2OH^\ominus$[5]:

$$Cl_2 + H_2O$$

$$k_1 = 11 \ s^{-1}$$

$$Cl_2OH^\ominus + H^\oplus \rightarrow ClOH + H^\oplus + Cl^\ominus$$

$$k_2 = 10^{10} \ M^{-1} s^{-1}$$

$$Cl_2 + OH^\ominus + H^\oplus$$

In aqueous alkaline solution, Cl_2 decomposes more or less rapidly to chloride deliberating oxygen depending on the conditions[6]:
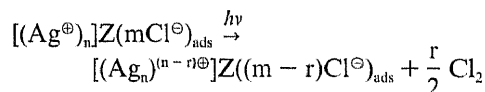
$$Cl_2 + H_2O + OH^\ominus \rightarrow 2\,Cl^\ominus + \frac{1}{2}\,O_2 + H_3O^\oplus$$
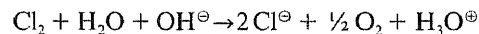
Tracer studies have revealed that, in addition to H_2O attack upon HOCl to form H_2O_2,

$$HOCl + 2\,H_2O \rightarrow Cl^\ominus + H_3O^\oplus + H_2O_2$$
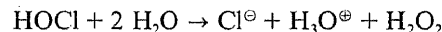
oxygen exchange between H_2O and HOCl occurs in hypohalite solutions[7].

The photo-chlorine evolution can be described as follows[3]:

$$[(Ag^\oplus)_n]Z(mCl^\ominus)_{ads} \xrightarrow{h\nu}$$
$$[(Ag_n)^{(n-r)\oplus}]Z((m-r)Cl^\ominus)_{ads} + \frac{r}{2}\,Cl_2$$

where Z represents the negatively charged zeolite lattice.

A study of the pH dependence of the photo-chlorine and of the photo-oxygen evolution from an aqueous silver zeolite A dispersion in presence of $Cl^\ominus$ revealed the result that at pH 4 a strong signal for chlorine can be observed which decreases with increasing pH and vanishes in the strongly alkaline region. A significant oxygen-signal can be observed only above pH 9. We assume that in slightly acidic to slightly alkaline environment hypochlorite is formed which, however, could not be detected with the oxygen- and the chlorine-sensitive sensors applied in these experiments[8].

As already mentioned, quantitative experiments of the photo-oxygen evolution in aqueous dispersions of silver zeolites have shown that the system exhibits spectral sensitization[1]. This «self-sensitization» was also observed in the case of photo-chlorine evolution[3]: a system which is insensitive to longer wavelengths shifts its photosensitivity to the visible range after having been irradiated with UV-photons. There was an argument that the photo-chlorine production with visible light is only possible immediately after exposure to UV-photons. This implies that the system must first store the energy of the UV-photons which then, together with visible light, induces the Cl_2 evolution. This argument which is unnecessary from an energetic point of view, has already become very improbable because of experiments reported by us[1, 3]. With the results shown in Fig. 1, however, we deliver unequivocal proof that it is wrong.

In the experiment reported 400 mg of $Ag^\oplus$-exchanged zeolite Linde 4A
$$Ag_{9.7}Na_{2.3}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 24\,H_2O$$
was dispersed in 100 mL of an 0.2M KCl solution. A pH of 3.8 was obtained by

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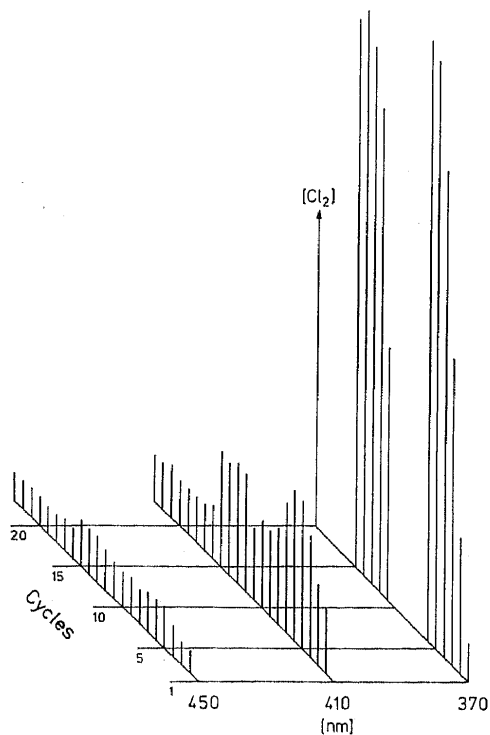Universität Bern
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Fig. 1. *Self-sensitization of the photo-chlorine evolution in an aqueous dispersion of silver zeolite A. The UV-illumination is omitted for some cycles.*

adding hydrochloric acid. The experiment consists of more than 20 illumination cycles, each starting at $\lambda = 450$ nm. The light flux was approximately 9 mW and the total illuminated area was 25 cm^2. At each wavelength indicated, the dispersion was irradiated for 5 min followed by a 25 min dark period. The photo-produced chlorine was completely removed by immersing a graphite rod in the dispersion between the exposures. Cl$_2$ diffuses very rapidly into graphite. The slit width of the monochromator corresponded to 30 nm. To make sure that no stray-light affected the observation, cut-off filters were employed: 389 nm for the 410 nm irradiation and 435 nm for the 450 nm irradiation. Each cycle took 2 h to be completed. For further experimental details we refer to previous publications[1,3]. The important property of the self-sensitization effect can be seen in the first cycle: no evolution of chlorine occurs above 400 nm and at 370 nm only a weak signal is detected. But already the second cycle shows photoactivity at longer wavelengths. After the 6th cycle the illumination at 370 nm was omitted for the four following cycles and switched on after the 10th and off again after the 15th cycle. The results reported in Fig. 1 show that after omitting the UV-exposure, the photo-chlorine evolution at 450 nm remains approximately constant thus proving that UV-photons are no longer necessary after an initial build-up period.
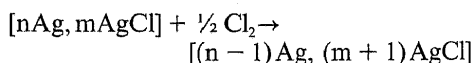
For an approval of the photo-chlorine production the large driving force of the back reaction Ag + ½ Cl$_2$→AgCl must be considered:

$$[Ag, AgCl|HCl\ (1M)|Cl^{\ominus}, ½\ Cl_2];$$
$$E^0 = 1.14\ V$$
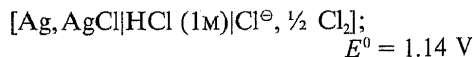
Despite of this high electrochemical potential, the recombination reaction does not occur. The following simple experiment illustrates it: a sheet of silver with an AgCl layer put into a HCl solution still shows the Ag/AgCl-potential after addition of Cl$_2$. This means that the electrode reaction

$$e^{\ominus} + [nAg, mAgCl] + ½\ Cl_2 \rightarrow$$
$$[nAg, mAgCl] + Cl^{\ominus}$$
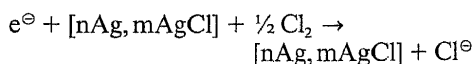
and the oxidation of the silver

$$[nAg, mAgCl] + ½\ Cl_2 \rightarrow$$
$$[(n-1)Ag, (m+1)AgCl]$$

are very slow, thus kinetically blocked. But as known from the high reversibility of the Ag/AgCl electrodes, the following reaction is very fast:

$$[nAg, mAgCl] \pm e^{\ominus} \rightarrow$$
$$[(n \pm 1)Ag, (m \mp 1)AgCl] \pm Cl^{\ominus}$$
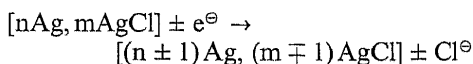
As a consequence, the photo-produced chlorine can easily be separated from the solution. Hence we do understand phenomenologically the fact that chlorine is rather slowly reduced in presence of an Ag/AgCl electrode or in presence of a partially reduced silver zeolite dispersion.

Based on these observations we have intended to construct a photoelectrochemical silver chloride cell with an open-circuit potential of 1.14 V. Photoelectrochemical experiments with silver chloride, silver bromide, and silver iodide have been published by several authors; see e.g.[10–14]. The photopotentials reported, however, were small with respect to the 1.14 V envisaged by us. Due to its low electrical conductivity, we have unfortunately not yet succeeded to realize a useful photoelectrode based on a silver zeolite, although such a device would be very interesting. But recently we have found that it is possible to realize such a cell by anodic oxidation of a silver sheet in a 0.2M KCl solution at pH 2 and a current density of 25 mA/cm^2 during several minutes. With two of these cells in series

we have achieved photoelectrochemical water decomposition, thus demonstrating that the principle really works[9]. In this paper we report significant improvement of the cell and demonstrate first experiments carried out with sunlight.

The principle of our device is sketched in Fig. 2A. The silver sheet with the photosensitive silver chloride is immersed in an acidic potassium chloride solution and connected via the resistor R with the graphite counter-electrode. As already explained, illumination of the silver chloride layer produces chlorine (reaction (a)). The discharge of the cell generating electricity follows reaction (b) at the silver electrode and reaction (c) at the counter-electrode.

(a) $AgCl \overset{h\nu}{\rightarrow} Ag + ½\ Cl_2$
(b) $Ag \rightarrow Ag^{\oplus} + e^{\ominus}$
(c) $½\ Cl_2 + e^{\ominus} \rightarrow Cl^{\ominus}$
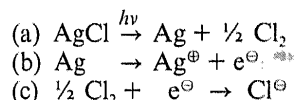
According to the accepted definition[15–17], a photogalvanic cell is a device where, in a homogeneous or heterogeneous photoreaction, products are formed, which can generate electricity at proper electrodes. The photoelectrochemical {Ag/AgCl‖Cl$^{\ominus}$/Cl$_2$} cell has to be classified therefore as a photogalvanic cell.

The photocurrent which can be delivered by such a cell depends on the rate of the Cl$_2$ production and on the electrode kinetics which is transport-controlled. At high enough Cl$^{\ominus}$ concentration the transport properties of the cell are dominated by Cl$_2$, however, the solubility equilibria of the silver chloride complexes must be taken into account. A good cell should therefore have a large photoactive surface and an optimal cell geometry. General studies on current-voltage and power characteristics of photogalvanic cells have been carried out by *Albery* and *Archer*[15, 18] and others[19]. These studies are based on a different type of systems than the photogalvanic {Ag/AgCl‖Cl$^{\ominus}$/Cl$_2$} cell and we have to find out which of these earlier results can be applied. For this reason we have designed the cell shown in Fig. 2B which helps to obtain preliminary information about important parameters, thus delivering an experimental basis for first optimization studies. A fine-meshed
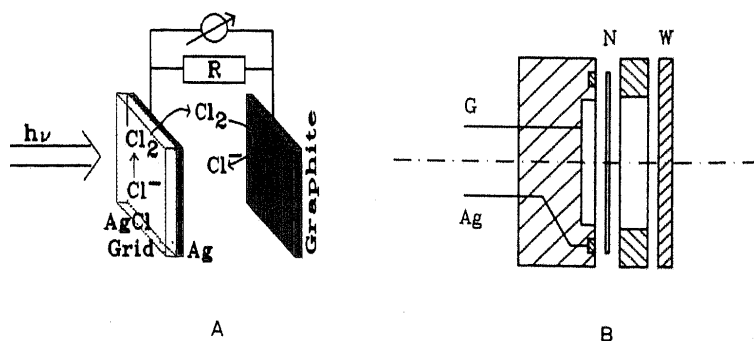

A   B

Fig. 2. *The photogalvanic {Ag/AgCl‖Cl$^{\ominus}$/Cl$_2$} cell: A) schematic diagram; B) construction plan.*
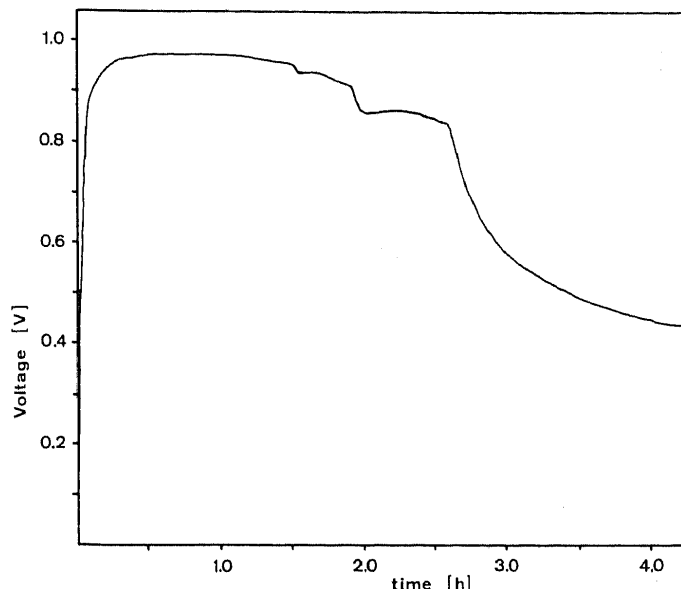
Fig. 3. Photopotential of the $\{Ag/AgCl\|Cl^{\ominus}/Cl_2\}$ cell.

silver net (360 mesh) N serves as silver electrode. A porous silver chloride layer is achieved by anodic oxidation of the silver net in a 0.2M KCl/1M HCl solution at a current density of 68 mA/cm² during 100 s (500 μeq). The distance between the graphite counter-electrode G and the Ag/AgCl electrode is about 1 mm. Ohmic contact between the graphite and a silver wire is realized by using conductive carbon cement (after *Göcke,* Neubauer Chemicals). The so prepared electrode G is poured in a block of araldit (Araldit D, hardening agent HY 951; 100:8) together with a silver contact Ag, consisting of a silver ring on which a silver wire is welded. Pressing the quartz window W, the spacer, the silver net, and the araldit block together seals the cell and provides ohmic contact between the net and the silver ring. The area of the active electrode is about
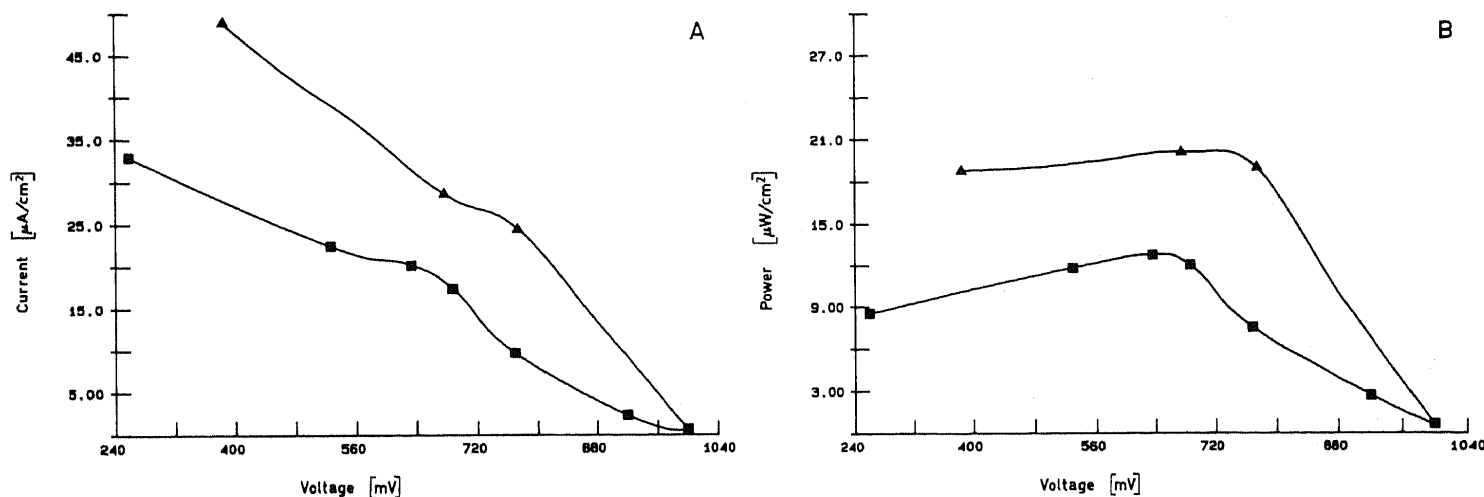

Fig. 4. Performance of the $\{Ag/AgCl\|Cl^{\ominus}/Cl_2\}$ cell: A) current/voltage diagram; B) power/voltage diagram (number of silver nets: 1 ■, 2 ▲).
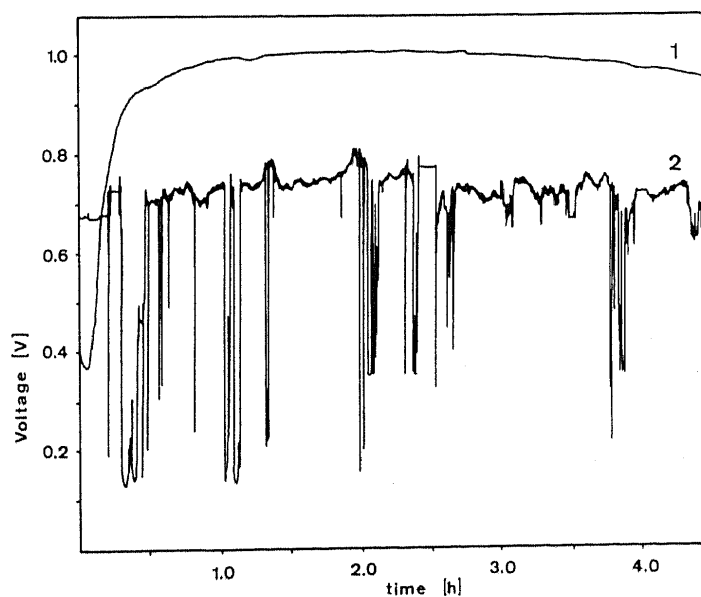

Fig. 5. Photopotential under solar irradiation: 1) photovoltage of the $\{Ag/AgCl\|Cl^{\ominus}/Cl_2\}$ cell; 2) relative solar intensity measured by a silicon cell.

0.8 cm² and the electrolyte consists of aqueous KCl + HCl solutions.

Fig. 3 shows a typical photopotential response of this cell. Illumination started at time $t = 0$ with a high-pressure mercury source (150 W), the infrared part of which was filtered by a 10 cm thick water cuvette. After 5 min of irradiation 90% of the maximum open-circuit potential was reached. The maximum potential observed in this experiment was 960 mV. It remained stable during 1 h and then decreased slowly. Decreasing the aperture, thus decreasing the light intensity, caused the breaks in the potential. At $t = 2.6$ h the aperture was completely closed. Photopotentials up to 1.05 V have regularly been obtained in other experiments. Playing with the HCl + KCl electrolyte we found pH = 0, 0.2M KCl, 1.0M HCl to be a good choice in conformity with the theoretical considerations given above. Varying the resistance R between the electrodes results in the current/voltage char-

acteristics and the power/voltage characteristics shown in Fig. 4. To get comparable results we prepared a new photoelectrode for each new value of the resistance. The maximum potential was reached and tabulated after an illumination time of about 15 min.

The maximum power density extrapolated to zero per cent transmission of the silver net was 17.1 µW/cm² at a cell potential of 630 mV. Our silver nets had a light transmission of about 25% and two of them, one behind the other, had a transmission of about 9%. When carrying out the experiments with the two silver nets, one behind the other, we observed a somewhat higher increase of power density than expected from the decreasing transmission, i.e. 21.3 µW/cm² at 730 mW.

Remarkable results have been obtained by exposing the cell to the sunlight. Curve 1 in Fig. 5 shows the open-circuit potential of the cell. It looks similar as in the laboratory experiments but it takes more time to reach the maximum potential. Interestingly enough, the system seems to be more stable and shows better performance when irradiated by sunlight than by the high-pressure mercury lamp. Curve 2 indicates the relative intensity of the sunlight registrated with a silicon sensor during the exposure of the photogalvanic cell. As can be seen from the fluctuations of the silicon cell response, the sky was not clear. When the sun vanished for even more than 5 min, there was no notable decrease of the potential which shows a special quality of the photogalvanic {Ag/AgCl‖Cl⊖/Cl₂} cell. It demonstrates the short-time energy storage capacity of the system.

After these encouraging results which hopefully help to change the idea that AgCl electrodes behave simply as semiconductors when irradiated[12, 20], we shall intensify our studies of the photogalvanic {Ag/AgCl‖Cl⊖/Cl₂} cell.

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Indazole: Photoleitfähigkeit und Oxidationspotentiale

Bernhard Albert*, Peter Neumann und Gerhard Hoffmann

Professor Helmut Dörfel zum 60. Geburtstag gewidmet

Abstract: In sensitized electrophotographic layers, excellent charge transport properties are exhibited by 2-(p-aminophenyl)indazoles (1). Corresponding 2-aminoindazoles (2) are ineffective. – Conclusions as to charge transport efficiency, which is effected via radical cations, are drawn from the oxidation potentials of the indazoles.

Elektrophotographische Schichten aus organischen Materialien gewinnen neben den herkömmlichen Silicium- und Selen-Photoleitern an Bedeutung, insbesondere für Kopierfolien[1–3] und elektrophotographische Offsetdruckplatten[3, 4]. Unter den möglichen Ausprägungsformen[1] haben in letzter Zeit die sogenannten homogen sensibilisierten amorphen Photoleiterschichten auf der Basis von Defektelektronenleitern besonderes Interesse gefunden. Diese Defektelektronenleiter sind niedermolekulare organische Verbindungen, vorwiegend p-Aminophenyl-Derivate[3]. Aus ihrer chemischen Struktur kann die Effizienz des Ladungstransports bisher nicht vorhergesagt werden, da allgemeingültige Struktur/Wirkungs-Beziehungen sowie Kenntnisse über den Einfluss der direkten Umgebung im molekularen Bereich noch nicht vorliegen. Es gibt allerdings einige wenige Regeln zumeist qualitativer Natur bezüglich bestimmter Strukturmerkmale sowie Zusammenhänge zwischen molekularen Parametern (wie Ionisations- oder Oxidationspotential, spektrale Absorption, Fluoreszenz, Polarisierbarkeit) und elektrophotographischen Eigenschaften[1–5].

Insbesondere für die industrielle Forschung stellt sich bei der Suche nach neuen Systemen mit verbesserten Eigenschaften die Aufgabe, Modellvorstellungen zu entwickeln, die eine Korrelation zwischen der Effizienz der Defektelektronenleitung in der elektrophotographischen Schicht und leicht messbaren charakteristischen Parametern der organischen Verbindungen ermöglichen.

Eine Möglichkeit scheint uns das Oxidationspotential der photoleitenden Verbindung $\bar{M}$ zu sein, das die Bereitschaft widerspiegelt, in das Radikalkation $M^{\oplus}$ überzugehen:

$$\bar{M} \rightleftharpoons M^{\oplus} + e^{\ominus}$$

Erst über dieses Radikalkation kann dann der Ladungsträgertransport in einem elektrischen Feld erfolgen (Hopping-Mechanismus)[9, 10]:

$$\bar{M} \cdots M^{\oplus} \cdots \bar{M} \cdots \bar{M} \rightarrow \bar{M} \cdots \bar{M} \cdots M^{\oplus} \cdots \bar{M}$$

Wir haben an den neuen Indazolderivaten 1[6] und 2 Photoleitung und Oxidationspotential[14] mittels Cyclovoltammetrie[11, 13, 15] untersucht.
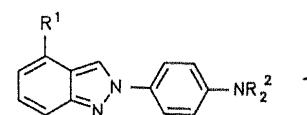
$R^1 = H, Cl; R^2 = C_2H_5, C_6H_5$

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