

Short communication

Electrooxidation of ascorbic acid on polyaniline and its implications to fuel cells

S.K. Mondal^a, R.K. Raman^b, A.K. Shukla^b, N. Munichandraiah^{a,*}

^a Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

^b Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Abstract

L-Ascorbic acid (AA) has been shown to undergo oxidation on polyaniline (PANI) without a platinum-group catalyst. A direct ascorbic acid fuel cell (DAAFC) has been assembled by employing an anode coated with PANI catalyst. From the experimental studies using cyclic voltammetry, amperometry and IR spectroscopy, it has been concluded that PANI facilitates the oxidation of AA. It has been possible to achieve a maximum power density of 4.3 mW cm^{-2} at a load current density of 15 mA cm^{-2} at 70°C . As both AA and PANI are inexpensive and environmental-friendly, the present findings are expected to be useful for the development of cost-effective DAAFCs for several low power applications.

Keywords: Ascorbic acid; Polyaniline; Electrooxidation; Fuel cell

1. Introduction

In the context of fast depletion of fossil fuel resources as well as the increase in atmospheric pollution, research and development activities on batteries and fuel cells have occupied great importance in recent years. Among several types of fuel cells, polymer electrolyte direct methanol fuel cells (DMFCs) are being projected for a variety applications ranging from micro-power to mega-power [1–3]. This is primarily because of feeding of a liquid fuel to the anode in a convenient way. Rapid miniaturization of electronic devices and expansion of their utility are likely to demand for further potential applications of DMFCs.

The attractive features of DMFCs are also due to a high theoretical energy density expected from methanol among several small organic molecules [4]. This is due to the transfer of six electrons per molecule during oxidation of methanol to CO_2 and H_2O . Furthermore, a regenerative DMFC, which is based on the concept of electrochemical reduction of CO_2 to CH_3OH and employing the latter as the fuel, sounds

more interesting as this is also related to address the global warming problem [5]. Despite of the advantages and interesting aspects involved in using methanol as the fuel for electrochemical energy conversion, the electrocatalyst used for the oxidation of methanol plays a crucial role. The best catalyst known for this reaction is Pt–Ru alloy [6]. However, for a wide-spread application of fuel cells, it is imperative to employ a non-platinum metal catalyst for cost reduction.

There are two approaches to handle the problem of reducing the usage of expensive platinum metal catalysts in fuel cells. One approach is to investigate alternate bi- or trimetallic catalysts employing on transition metals, or modified conducting polymers [7]. The other approach is to investigate alternate fuels which can undergo oxidation on inexpensive catalysts [8]. In the latter approach, ascorbic acid (AA), which is a biologically important compound and inexpensive, is investigated as the fuel in the present work. In comparison with methanol, AA is a solid, slightly more expensive and provides lower energy density. However, studies using AA as the fuel are interesting as AA is soluble in acidic aqueous solutions to make sufficiently concentrated solutions, and it can undergo electrooxidation on an inexpensive non-noble metal catalyst,

* Corresponding author. Tel.: +91 80 22933183; fax: +91 80 23600683.
E-mail address: muni@ipc.iisc.ernet.in (N. Munichandraiah).

whereas the oxidation of methanol requires an expensive catalyst material.

Although electrooxidation of AA has been a subject of several investigations [9–11], these studies have involved Pt-group metals as the catalysts. AA has been suggested as a promising fuel for fuel cell application [12], and a study on direct ascorbic acid fuel cell (DAAFC) employing several Pt-group metals as the catalysts have been reported recently [13]. In this study [13], the oxidation of AA has been evaluated by cyclic voltammetry on glassy carbon electrodes, which were coated with Pt, Ru, Pd, Ir, Pt–Ru blacks. The oxidation of AA has been shown to take place on these catalysts at potentials close to the theoretical value. But these catalysts show different degrees of catalytic effect towards the oxidation of AA. The performance of DAAFCs has been evaluated by circulating an aqueous solution of AA through the anode and measuring current–potential characteristics. It has been shown the performance of the DAAFC employing Pd catalyst is superior in relation to the other catalysts.

In a recent study [14], it has been shown that the oxidation of AA occurs on a polyaniline (PANI) covered Ni substrate in the absence of any Pt-group metal. The focus of the present study is to further investigate the use of oxidation of AA on PANI as the catalyst for fuel cells, where the anode reaction does not involve any Pt-group metal. Since PANI is an inexpensive conducting polymer, it is anticipated that the present study would invoke significant interest in the area of fuel cells research and development.

2. Experimental

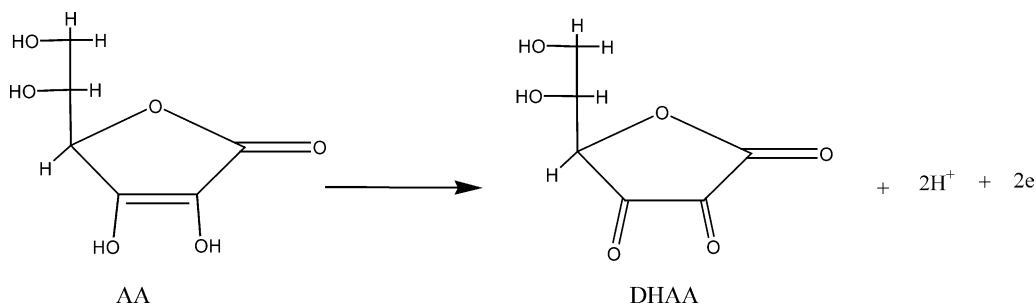
Analytical grade chemicals, vacuum distilled aniline and double-distilled water were used in all experiments. Polymerization of aniline to PANI was carried out by both chemical and electrochemical oxidations. For chemical preparation, aniline was dissolved in H_2SO_4 (0.5 M), and a solution of $\text{NH}_4\text{S}_2\text{O}_8$ (1 M) was added drop-wise while stirring the solution using a magnetic bar. The PANI powder thus formed was filtered, washed copiously with 0.5 M H_2SO_4 and dried at about 60°C under vacuum. For electrochemical preparation of PANI, a stainless steel (SS, commercial grade, 304) substrate was polished, etched in dilute H_2SO_4 and washed. An electrochemical cell was set up in a glass container, which had provision to introduce the SS working electrode, a Pt auxiliary electrode and a reference electrode. A saturated

calomel electrode (SCE) was used as the reference electrode. An electrolyte solution of 0.5 M H_2SO_4 consisting of aniline (0.5 M) was taken inside the cell and the SS electrode was cycled between -0.2 and 1.2 V versus SCE at a sweep rate of 100 mV s^{-1} . A film of PANI forms on the SS electrode, and its thickness increases by repeating the potential cycles several times. The PANI/SS electrode was washed copiously with 0.5 M H_2SO_4 and stored in the same solution for further experiments. The PANI/SS electrode was used for single electrode studies, whereas the chemically precipitated PANI was used for fuel cell studies.

A laboratory scale DAAFC was assembled using carbon block current collectors and a membrane electrode assembly (MEA). For preparation of the anode, PANI (90 wt.%) and Nafion suspension (10 wt.%) were taken in isopropyl alcohol and subjected to sonication for intimate mixing. The suspension was brushed on a non-wettable Toray carbon paper (TGPH 090) of size $4\text{ cm} \times 4\text{ cm}$. The solvent was allowed to evaporate and dried at open air. Several such electrodes were prepared by varying the loading of PANI between 15 and 60 mg. Using a similar procedure, Pt coated cathodes were prepared. A film of Nafion 117 was hot pressed at about 125°C with a cathode and a dummy carbon paper anode, which was subsequently replaced by a PANI coated carbon paper. Hot pressing with the PANI anode was avoided since PANI loses its electrochemical activity towards the oxidation of AA due to thermal degradation. The MEA was in turn sandwiched between two corrugated carbon blocks, which had provision to circulate the anolyte solution at the anode and to pass oxygen gas at the cathode. Cyclic voltammetry and chronopotentiometry of PANI/SS was carried out using a EG&G potentiostat/galvanostat model Versastat. Current–voltage measurements of fuel cells were performed using a home-made galvanostatic circuit. IR spectra were recorded by a Perkin-Elmer FT-IR 1000 spectrometer.

3. Results and discussion

Rueda et al. [15] have studied the oxidation of AA on a gold electrode over a wide pH range. Products of the reaction have been identified by chronoamperometry and the total number of electrons taking part in the oxidation has been estimated to be 1.9. On the basis of their results, the following mechanism has been proposed.



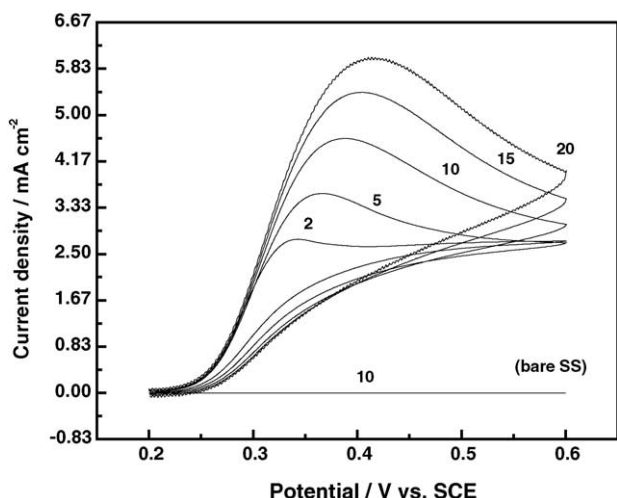


Fig. 1. Cyclic voltammograms recorded in a 50 mL solution of 10 mM Ascorbic acid + 0.5 M H₂SO₄ with a polyaniline coated stainless steel electrode at different scan rates (mVs⁻¹) indicated on each trace. A similar experiment was repeated for bare stainless steel electrode with a scan rate of 10 mVs⁻¹.

The formation of dehydroascorbic acid (DHAA) takes place via a radical anion intermediate, monodehydroascorbic acid from AA. The DHAA undergoes a hydration reaction characteristic of the carbonyl group to form DHAA·H₂O, which is electroinactive. Accordingly, the electrooxidation of AA is irreversible [15]. Cyclic voltammograms recorded at several sweep rates (v) using a PANI/SS electrode in 0.5 M H₂SO₄ consisting of 0.1 M AA are shown in Fig. 1. There is an oxidation current peak in the potential range between 0.3 and 0.4 V versus SCE, and the peak current increases with square root of sweep rate. Also, there is a shift in peak potential with increase in sweep rate. These features together with the observations of an increase in peak current with an increase in concentration of AA (not shown) and the absence of cathodic current peak confirm the irreversible oxidation of AA on PANI/SS electrode. Furthermore, as the cyclic voltammograms do not appear on a bare SS electrode (Fig. 1), it is concluded that the PANI catalyzes the oxidation. A continuous oxidation of AA in 0.5 M H₂SO₄ was carried out at different current densities on a PANI/SS electrode while stirring the electrolyte with a magnetic bar. The variation of potential during about 24 h of electrolysis is shown in Fig. 2. The electrode potential is fairly constant at current densities lower than 33 mA cm⁻² suggesting that the PANI is stable for continuous electrooxidation of AA. Furthermore, there is an increase in potential by increasing current density. The relationship between current density and potential follows Tafel relationship as shown in Fig. 3, and the Tafel slope obtained is 0.370 V decade⁻¹.

The electrooxidation of AA on PANI is further established by recording an IR spectrum of the electrolyte after prolonged electrolysis. An electrolyte of 1 M AA in 0.5 M H₂SO₄ was electrolyzed using a PANI/SS anode at a current density of 50 mA cm⁻² for a duration theoretically required for com-

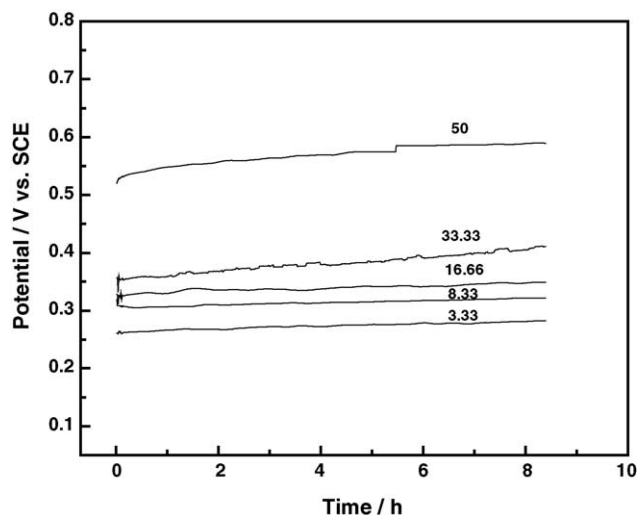


Fig. 2. Chronopotentiometry experiments performed with a polyaniline coated stainless steel electrode in 20 mL solution of 1 M ascorbic acid + 0.5 M H₂SO₄ at different current density values (mA cm⁻²) indicated on each trace.

plete oxidation of AA to DHA. The spectra of the electrolyte before and after completing the electrolysis are shown in Fig. 4. The intense band at 1700 cm⁻¹ for both AA and DHA is attributed to stretching vibration of C=O carbonyl group [16,17]. The band at 1780 cm⁻¹ due to C=O group [16] is clearly developed as a peak in DHA. The presence of a band at 1800 cm⁻¹ due to C=O group (Fig. 4 curve b), which is absent in Fig. 4 curve (a) is a clear indication for the formation of DHA. This band is attributed to the open bi-cyclic form of hydrated DHA. Furthermore, the band at 1150 cm⁻¹ due to asymmetric O-C-C stretching is clearly present in the spectrum of DHA (Fig. 4 curve b). These results support the electrochemical results obtained as described above for oxidation of AA on PANI as the catalyst.

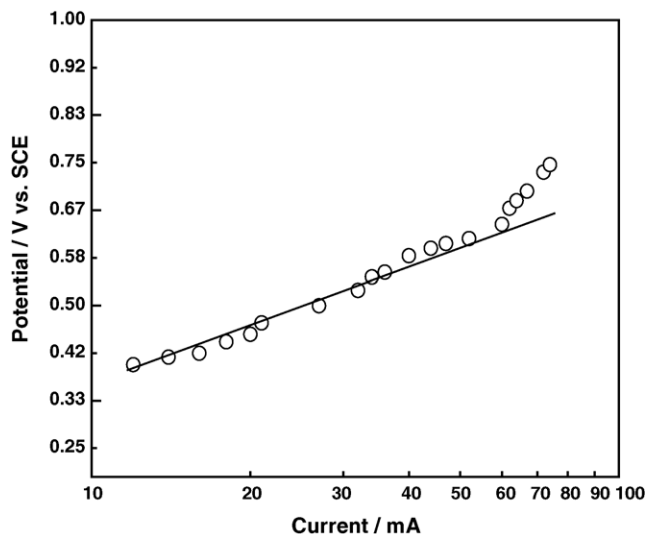


Fig. 3. Steady state polarization data obtained with a polyaniline coated stainless steel electrode (area = 0.6 cm²) in 1 M ascorbic acid + 0.5 M H₂SO₄.

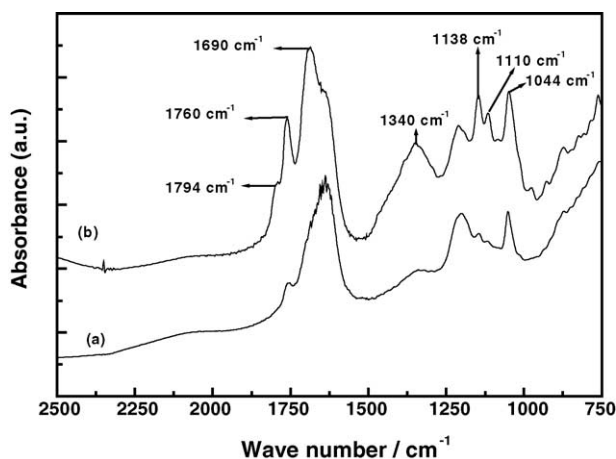


Fig. 4. IR spectra of ascorbic acid (a) before and (b) after oxidation in 0.5 M H_2SO_4 .

Several DAAFCs were assembled by fabricating the anode with varying PANI loading levels, namely, 15, 35 and 60 mg cm^{-2} . The performance of these cells were evaluated at different load current densities. It was found that the optimum performance was obtained with 35 mg cm^{-2} of PANI as the anode catalyst. At the other loading levels, the performance of the cells was inferior. The performance of the DAAFC with 35 mg cm^{-2} of PANI was evaluated by loading it with different values of current and measuring the corresponding voltages. The procedure was repeated at different temperatures from ambient to 70°C . The polarization data are shown in Fig. 5(a). At all temperature, there is a decrease in voltage from the open-circuit value of 0.5 V with an increase in current density. At a current density of 10 mA cm^{-2} , the cell voltage decreases to about 0.1 V at ambient temperature. However, there is a decrease in polarization with an increase in temperature. For instance at 70°C , the cell voltage is 0.35 V at 10 mA cm^{-2} . Alternately, a current density of 22 mA cm^{-2} is required at 70°C to decrease the voltage to 0.1 V. These data suggest that the DAAFC is useful in a wide temperature range. However, it may be noted that PANI undergoes deterioration at temperatures higher than 100°C . Therefore, $70\text{--}80^\circ\text{C}$ may be considered as a safe upper limit of temperature for optimum performance of DAFC. Fig. 5(b) presents power density versus current density curves at several temperatures. At 70°C , a maximum power density of 4.3 mW cm^{-2} is obtained at a current density of 15 mA cm^{-2} . There is a decrease in these parameters with a decrease in temperature.

The performance of the DAAFC in the present work may be evaluated by comparing the results with those reported in the literature for DAAFC as well as DMFC. A maximum power density of 6 mW cm^{-2} at a current density of 35 mA cm^{-2} has been reported for DAAFC with Pd as the anode catalyst at ambient temperature. In the present work, on the other hand, a maximum power density of 4.3 mW cm^{-2} is obtained at a current density of 15 mA cm^{-2} at 70°C . Al-

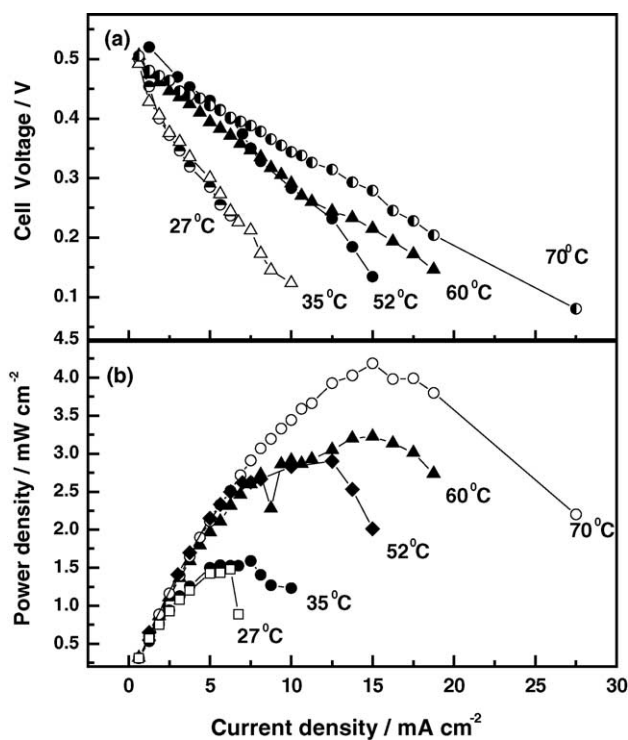


Fig. 5. (a) Polarization data and (b) power density versus current density data of DAAFC at different temperatures.

though these values are lower, the present DAAFC is shown to perform with an inexpensive conducting polymer, namely, polyaniline as the anode catalyst.

The DMFC is well studied and extensively reported. The best known catalyst for methanol oxidation is Pt–Ru alloy. A maximum power density of 180 mW cm^{-2} at 90°C has been reported [18]. This value is higher than the values obtained in the present study. Nevertheless, DAAFC is expected to be useful for micro-power applications where cost factor is an important criterion. Furthermore, the operation of DMFC is plagued with the problem of methanol cross-over, which affects the long term performance of the fuel cell [19,20]. By contrast, in the case of DAAFC, it would be difficult for ascorbic acid molecules to pass through the polymer electrolyte membrane due to their larger size in relation to methanol molecule.

In the recent years, there has been interest in the literature on bio-fuel cells [21–25]. A glucose–oxygen bio-fuel cell was studied by the engineering of the anode and cathode with bio-catalytic monolayer interfaces that enable the operation of the bio-fuel cell without separating the electrodes [21]. A miniature bio-fuel cell using oxidation of glucose on glucose oxidase as the catalyst with a power density of $64 \mu\text{W cm}^{-2}$ at 23°C has been reported [22]. In similar reports [23–25], miniature bio-fuel cells with low power densities have been studied. The present study on DAAFC may also be categorized as a bio-fuel cell because of biological importance of ascorbic acid.

4. Conclusions

The DAAFC described in the study employs PANI as the catalyst. The PANI is non-toxic, inexpensive, and a stable conducting polymer, which can be synthesized by simple chemical and electrochemical routes. Ascorbic acid is also inexpensive, biologically important and environmentally compatible compound. Although a Pt catalyst is used for reduction of O₂ at the cathode, an attempt is made in the present study for avoiding a noble metal catalyst for the anode.

References

- [1] N.M. Markovic, T.J. Schmidt, V. Stamenkovic, P.N. Ross, *Fuel Cell* 1 (2001) 105.
- [2] A.K. Shukla, R.K. Raman, *Annu. Rev. Mater. Res.* 33 (2003) 155.
- [3] A. Hamnett, in: R.G. Compton, G. Hancock (Eds.), *Chemical Kinetics*, vol. 37, Elsevier, Amsterdam, 1999, p. 593.
- [4] R. Parson, T. Van der Noot, *J. Electroanal. Chem.* 257 (1988) 1.
- [5] G.K.S. Prakash, G.A. Olah (personal communication).
- [6] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. Laconti, J. Kosek, G.K.S. Prakash, G.A. Olah, *J. Power Sources* 47 (1994) 377.
- [7] C.H. Yang, T.C. Wen, *Electrochim. Acta* 44 (1998) 207.
- [8] J.T. Muller, P.M. Urban, W.F. Holderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, *J. Electrochem. Soc.* 147 (2000) 4058.
- [9] S. Dong, G. Che, *J. Electroanal. Chem.* 315 (1991) 191.
- [10] M. Petersson, *Anal. Chim. Acta* 187 (1986) 333.
- [11] J. Wang, N. Naser, L. Angnes, H. Wu, L. Chen, *Anal. Chem.* 64 (1992) 1285.
- [12] K. Nobuyuki, Various fuels and their uses in fuel cells, in: K. Nobuyuki, U. Minoru (Eds.), *Chokogata Nenryo Denchi no Kaihatsu to Kongo no Tenbo* (Jpn.), Shi Emu Shi Shuppan, Tokyo, Japan, 2003, p. 196.
- [13] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazakiand, T. Kobayashi, *Electrochem. Solid State Lett.* 6 (2003) 257.
- [14] K. Rajendra Prasad, N. Munichandraiah, *Anal. Chem.* 74 (2002) 5531.
- [15] M. Rueda, A. Aldaz, F.S. Burgos, *Electrochim. Acta* 23 (1978) 419.
- [16] X. Xing, I.T. Bae, M. Shao, C.C. Liu, *J. Electroanal. Chem.* 346 (1993) 309.
- [17] K.B. Kokoh, F. Hahn, A. Metayer, C. Lamy, *Electrochim. Acta* 47 (2002) 3965.
- [18] A.S. Arico, P. Creti, E. Modica, G. Monforte, V. Baglio, V. Antonucci *Electrochim. Acta* 45 (2000) 4319.
- [19] M.K. Ravikumar, A.K. Shukla, *J. Electrochem. Soc.* 143 (1996) 2601.
- [20] N. Munichandraiah, K. McGrath, G.K.S. Parakash, R. Aniszfeld, G.A. Olah, *J. Power Sources* 117 (2003) 98.
- [21] E. Katz, I. Wilner, A.B. Kotlyar, *J. Electroanal. Chem.* 479 (1999) 64.
- [22] T. Chen, S.C. Barton, G. Binyamin, Z. Gao, Y. Zhang, H.H. Kim, A. Heller, *J. Am. Chem. Soc.* 123 (2001) 8630.
- [23] N. Mano, F. Mao, A. Heller, *J. Am. Chem. Soc.* 124 (2002) 12962.
- [24] U. Schroder, J. Nießen, F. Scholz, *Angew. Chem. Int. Ed.* 42 (2003) 2880.
- [25] N. Mano, F. Mao, A. Heller, *J. Am. Chem. Soc.* 125 (2003) 6588.