

In situ EPR investigation of polymer electrolyte membrane degradation in fuel cell applications

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Abstract

The main long-term purpose of this investigation is a profound understanding of the degradation mechanisms and the identification of fuel cell operating conditions and polymer electrolyte membrane properties which warrant a long lifetime and more reliable behaviour in general. The work involves the development and application of electron paramagnetic resonance (EPR) electrochemistry techniques to study polymer proton exchange membrane degradation in fuel cell applications. As a first step, a miniature cell that can work in a cavity of an X-band EPR spectrometer was built. This is the first report of an in situ fuel cell in an EPR spectrometer. We plan to identify different organic radicals which form in the running cell as intermediates of the degradation reactions. The objects of our research are different types of ionically, covalently, and covalent–ionically cross-linked polyarylether blend membranes.

It is demonstrated that tuning of the microwave cavity with a running fuel cell inside is possible, and a pronounced single-line EPR signal is observed. The signal has a *g*-value of 2.0030, thus it probably originates from the electrode material that is 0.00–2.00 mg/cm² Pt on Vulcan XC-72 E-Tek. Its behaviour depends strongly on the fuel cell conditions. It is interesting to note that when the cell is fed with oxygen and hydrogen, the signal intensity diminishes considerably, both under open circuit and under closed circuit conditions. This phenomenon is observed for different membrane types. When the gases are switched off the signal intensity is restored with a characteristic time of 1–2 h. For different membranes, this time differs. In general, water plays a very important role in the observation of EPR-spectra from the in situ fuel cell. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The proton-conducting membrane is the key component of a fuel cell system, because only extremely stable membranes can withstand the harsh chemical and physical environment, which includes active noble metal catalysts, temperatures which can exceed 100 °C, aggressive fuels and their partial oxidation products, aggressive oxidants, and the formation of reactive radicals. So, for a long and reliable operation the polymer membrane should have thermal and hydrolytic stability (100 °C), oxidative and reductive stability.

A localisation of the degradation would open the possibility to elucidate a mechanism and to prevent degradation by selective precautions. It was shown that HO• and HO₂• radicals originating from oxygen diffusion through the membrane and incomplete reduction at the fuel cell

anode are responsible for these degradation reactions [1]. Evidence for it are the formation of H₂O₂ as detected in product water, and other well known degeneration processes of polymers in general [2–5].

By combining the gas cross-over results and the long-term stability data it was shown that the rate of degradation increases with increasing gas cross-over [6]. This indicates that the stability of the highly cross-linked membranes is not only caused by cross-linking of the polystyrene chains, which slows down the loss of –SO₃H from the membranes, but also by reduced gas cross-over and, therefore, reduced HO₂• formation. High degrees of cross-linking (more than 12%) could improve the stability, however, the simultaneous increase of membrane resistance might not be tolerable [7]. The optimum membrane thickness which, as a compromise between gas cross-over and resistance, must be found.

Oxygen molecules diffuse through the membrane and as a result of incomplete reduction form active radicals on the platinum catalyst. These can attack the membrane material [8,9]. The dominating reaction in degradation processes of

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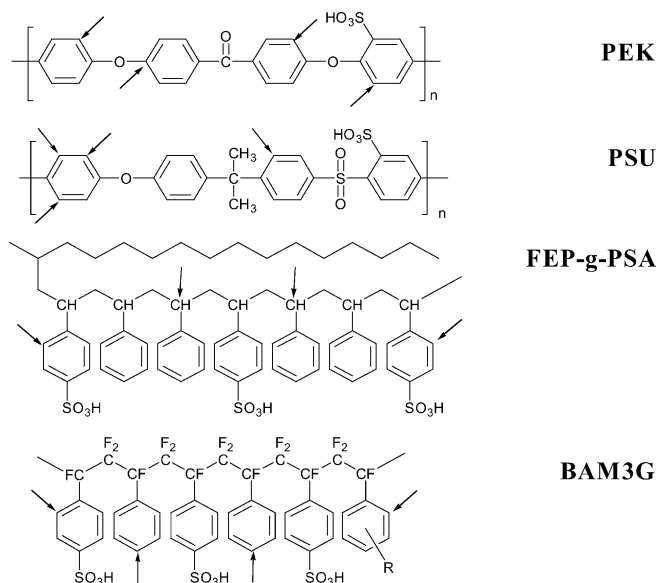


Fig. 1. Possible sites for HO• radical attack (arrows) on various polymers used for proton-conducting membranes.

unsaturated polymers is the addition of HO• to the aromatic rings, preferentially in the *ortho* position to alkyl- and RO-substituents (since in sulfonated PS, PSU, PEK and FEP-g-PSA the *para* position is substituted and thus blocked) [10]. It demonstrates the combined *ortho* activation by these substituents and the *meta*-directing effect of the SO₃ group in electrophilic addition reactions. Fig. 1 shows typical sites for HO• radical attack.

The crucial point is the acid-catalysed water elimination from hydroxycyclohexadienyl adducts. This process requires the presence of labile benzylic α-H atoms, thus it is not relevant for PSU or PEK type membranes but important in the case of FEP-g-PSA. In an endothermic process this can lead to chain scission ('reverse polymerisation') and thus to loss of –SO₃H groups. When water is eliminated from cyclohexadienyl radicals in poly(styrenesulfonate), radical intermediates are identified by UV-Vis and EPR under acidic conditions [11]. They can act as centres of degradation reactions in all of the newly developed polymers. The lack of α-H atoms certainly contributes to a much better long-term behaviour [1].

Another crucial point is the C–O–C bond breaking, initiated by attack of HO•. This degradation mechanism is of relevance for the polymers with phenoxybenzene ether bridges like PSU or PEK. However, phenoxyl radicals are not observed at pH < 5, so the degradation may be avoided as long as the local pH is sufficiently low [10].

Under fuel cell operating conditions there is plenty of ³O₂ present, at least near the cathode. It was proposed that ³O₂ reacts with cyclohexadienyl radicals under formation of peroxy radicals, which finally leads to bond breaking within the aromatic rings [12]. In the presence of both HO• radicals and oxygen, complete degradation of the aromatic rings can be achieved within a few hours. In view of this, the

saturated and perfluorinated Nafion® which is much more inert has an inherent advantage over the new membranes based on aromatic hydrocarbons. However, perfluorinated membranes also have some severe disadvantages, including the high price and the high methanol permeability in direct methanol fuel cells which leads to cell potential reduction. So, the needs for new membrane materials are extremely high today. Among the new approaches are different nonfluorinated ionically, covalently and covalent–ionically cross-linked polyaryl-blend membranes [13–17]. The stability of these materials must be investigated.

Traditionally, fuel cell systems were investigated mainly by means of electrochemistry. But it would be highly desirable to have additional methods available for obtaining selective information of a running fuel cell. It is our aim to develop an in situ EPR cell to monitor catalytic reactions and oxidative membrane degradation processes as a function of the electrochemically well characterised state of a running fuel cell. Here we present the first results of the programme.

2. Experimental

A miniature fuel cell which can operate in a resonator of an X-band EPR spectrometer (maximum diameter 11 mm) was constructed. Some indispensable requirements to fuel cell material are inertness and stability, and low dielectric losses under fuel cell running conditions. According to these requirements, teflon was chosen as a body material for the cell. Despite some very useful properties, teflon has also a disadvantage: the material is relatively soft and cannot be pressed too hard.

The in situ fuel cell consists of two half-cylinders (Fig. 2a). Each half-cylinder has an indentation where the active part of the fuel cell is situated. This active part includes Pt mesh as a spacer to allow gas distribution and at the same time provides electrical contact, gas diffusion electrodes and the polymer electrolyte membrane. There are gas feeding channels inside the half-cylinder in order to provide the cell with oxygen and hydrogen. To control current and voltage the electrodes are connected with a potentiostat (LB 95AR) by silver wires located in the gas channels. Fig. 2b shows a photo of the in situ fuel cell and the resonator of an X-band EPR spectrometer.

Gas diffusion electrodes are Vulcan XC-72 E-Tek electrodes with different Pt content (0.00–2.00 mg/cm²).

As polymer electrolyte membranes we used Nafion 115 and two novel types of covalently and ionically cross-linked composite membranes with improved properties in hydrogen and direct methanol fuel cell applications [13,18].

The periphery for the fuel cell consists of gas sources (H₂ and O₂), gas flow control system (MKS 247 C) and humidifiers in order to moisten gases before they enter the cell. Gas velocities were 10 cm³/min, and 20 cm³/min for oxygen and hydrogen, respectively.

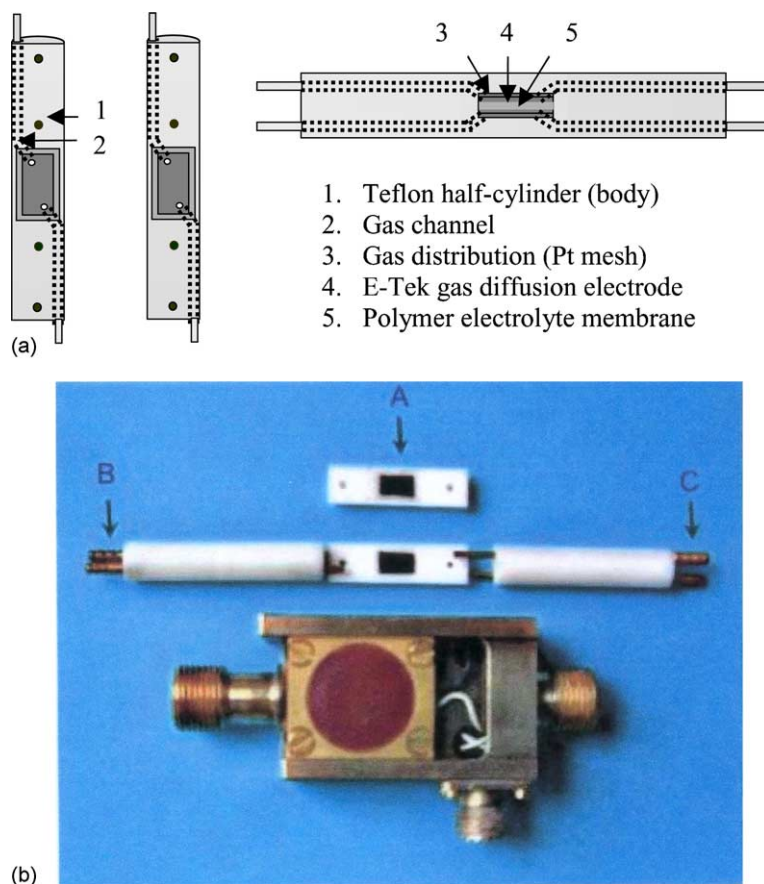


Fig. 2. (a) Schematic drawing of a fuel cell for in situ operation in an EPR spectrometer. (b) In situ fuel cell and resonator of X-band EPR spectrometer. A: active area (fuel cell part, black), B: gas feeding (O_2 and H_2 channels), and C: gas exhaust.

ESR spectra were recorded with a Bruker EMX X-band spectrometer. g -values were calculated relative to the Bruker[®] weak pitch sample ($g = 2.0028$). They are accurate to ± 0.0002 units. The microwave power was held at 0.320 mW, the modulation amplitude was 1–5 G. Ex situ low-temperature experiments were performed in a special cooling unit, which can operate in the temperature range of 1.8–300 K.

3. Results

The described fuel cell can be operated inside the microwave resonator of the EPR spectrometer. In spite of the unfavourable presence of water and electrically conducting materials, it is possible to record EPR-spectra. Typical spectra under different running conditions are shown in Fig. 3. The fuel cell was fed either with both hydrogen and oxygen, only with hydrogen, only with oxygen, or with no gases. These changes in feeding conditions lead to significant effects on the signal. Quite unexpectedly, the intensity decreases during fuel cell operation under both open circuit and closed circuit conditions. All three membrane types were tested in such experiments, and the behaviour was found to be quite similar for all of them. The signal

has a g -value of 2.0030 and originates from the electrode material.

To investigate how the signal depends on the nature of the electrode material, spectra from electrodes with different Pt content were recorded at room temperature. Fig. 4 displays the signal intensity as a function of Pt content and relative intensities in humid and dry air conditions. These experiments were performed ex situ. The signal intensity shows a consid-

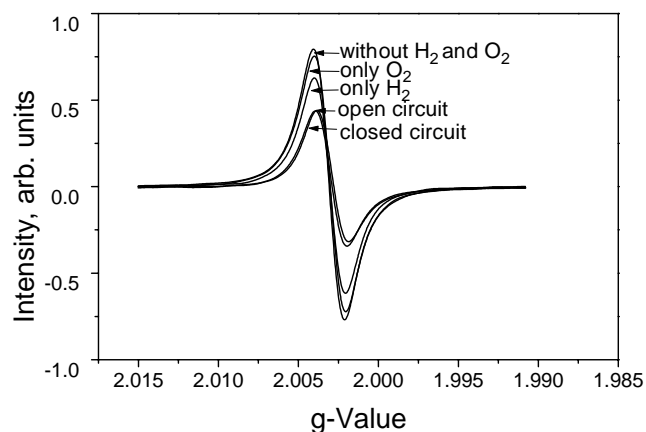


Fig. 3. EPR-signal of the fuel cell at different running conditions. Electrodes: 0.6 mg Pt/cm^2 .

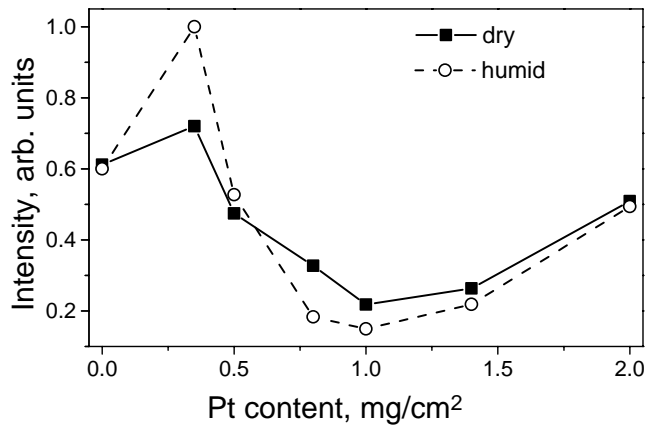


Fig. 4. Signal intensity as a function of Pt content in dry and in humid air.

erable dependence on the Pt content and on the air humidity. The sample with 0.35 mg/cm^2 Pt shows a more than five times greater spin content than the sample with 1.00 mg/cm^2 Pt. For the samples with 0.35 and 0.50 mg/cm^2 Pt content, the signal grows in humid air conditions, whereas for the other materials the presence of water reduces the intensity.

Fig. 5 depicts the signal width as a function of temperature for electrode materials with no Pt, and with 0.35 and 1.00 mg/cm^2 Pt content. Samples with and without Pt show a fundamentally different behaviour. Pure carbon has a very broad line at temperatures up to 55 K . With increasing temperature it narrows by a factor of more than 2 compared with low temperature. Line widths obtained with Pt loaded samples do not depend so strongly on the temperature and broaden with increasing temperature. From 150 K up to room temperature, the line widths from all three samples are relatively similar.

In order to investigate the influence of water on the signal, experiments with dry and humid feed gases were carried out. The fuel cell was fed with humid hydrogen and oxygen until a stationary state of the signal was achieved. As a rule, the necessary time for this was approximately 1 h or

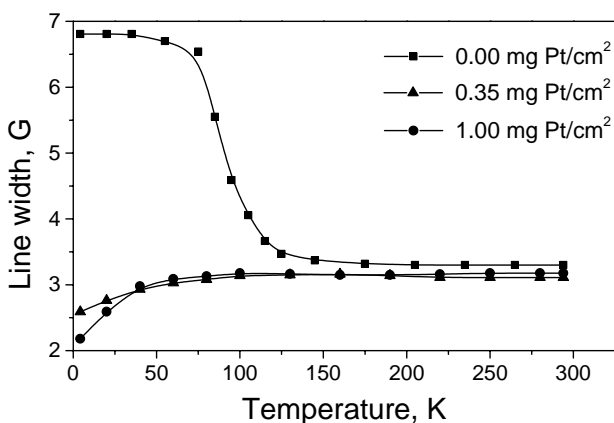


Fig. 5. Peak-to-peak line width for electrode materials with no Pt, and with 0.35 and 1.00 mg/cm^2 Pt content.

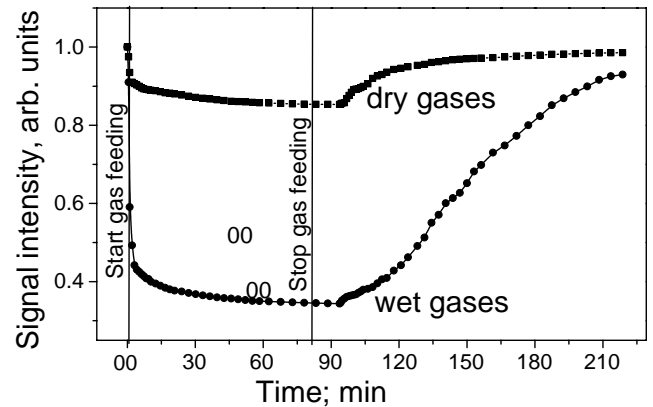


Fig. 6. Intensity of the EPR signal as a function of time with dry and humidified gas feeding. Electrodes: 0.6 mg Pt/cm^2 .

a bit more. Later-on the gases were switched off and the signal behaviour was observed further for 2 h . Then, this experiment was repeated with dry oxygen and hydrogen. Fig. 6 shows the signal intensity for these two cases. It was found that the presence of water in the gases decreases the signal drastically, independently of the membrane type.

4. Discussion

4.1. Ex situ investigation of the electrodes

The signal was identified to originate from electrode material and belongs to conduction electrons in carbon. It was shown earlier, that carbon materials have unpaired electrons which can be detected by means of EPR techniques. The number of free electron spins for carbon materials often lies in the range of 10^{19} to 10^{20} spins/g [19–21].

The fuel cell signal has a g -value of 2.0030 which is also typical for carbon materials (1.995 – 2.0031) [20,22], and it is almost symmetric. The electrode material itself without Pt has a significant number of unpaired electrons. With increasing Pt content, the signal intensity grows and has a maximum at a Pt content of 0.35 mg/cm^2 (Fig. 4). Then, the intensity goes down.

The peak-to-peak line width behaviour is completely different for electrode samples with and without Pt. For the carbon material in the absence of Pt, the signal narrows with increasing temperature from 6.808 to 3.300 G , whereas for electrodes with Pt it becomes broader and reaches 3.176 and 3.110 G for 0.35 and 1.00 mg/cm^2 Pt loadings, respectively, at high temperatures. This behaviour can be explained in terms of a change in the nature of the radical centres. In the case of pure carbon, its conduction electrons are responsible for the EPR signal, but in the presence of Pt clusters spins migrate to the surface and can be captured by these clusters, thus it is likely that electrons locate mainly in the Pt clusters. At low Pt loadings, there are a number of small Pt clusters on the surface, and each cluster may have an un-

paired electron. With increasing Pt content, particles grow and can merge. So, its number decreases and unpaired spins recombine. In general, this leads to a decrease of unpaired spins and thus of signal intensity.

Under fuel cell running conditions, water is an inseparable and very important part of the system. Its presence has a great influence on the EPR signal from electrode material. Water in the probe can significantly reduce the sensitivity of an EPR spectrometer and cause a signal decrease. Another potential influence lies in the adsorption of water molecules on the catalyst surface and interaction with surface species. At present, it is not clear what the interaction of water with the platinum clusters is that leads to the reduction of the signal. Fig. 4 shows the EPR-signal intensity for different electrode materials in dry and humid (saturated with water vapour at 25 °C) environment. Water vapour increases the number of unpaired electrons in the system for the sample containing 0.35 and 0.50 mg/cm² Pt, but when the Pt content further increases the intensity goes down in humid air.

4.2. *In situ* fuel cell studies

Fig. 3 shows EPR spectra at different fuel cell running conditions. In this case, electrodes have 0.60 mg/cm² Pt. The behaviour of the signal depends strongly on the fuel cell conditions. One can see that instead of growth under open circuit and closed circuit conditions the signal intensity decreases.

This surprising result can be explained at least partly in terms of water formation in the fuel cell during its operation. Water vapour also enters the cell with feed gases which are moistened in humidifiers. As it was shown in the above *in situ* experiments, water significantly reduces the signal from electrode material.

In order to check this proposal, the following test experiment was made. The fuel cell was fed with humidified hydrogen and oxygen and then for comparison reasons under the same conditions with dry gases. Fig. 6 shows the time dependence of the signal intensity for these two cases. Under humid conditions, the signal loses up to 65% of its intensity, whereas under dry conditions it loses only 15%. It should be noted that the position and the shape of the signal do not change.

On starting the gas feeding, the intensity goes down rapidly, and approximately in 60 min it reaches a steady level. When the gases are switched off, the signal recovers over approximately 2 h. The intensity behaviour presented in Fig. 6 is quite common for the different types of membranes and may be attributed to the electrode properties (Fig. 4).

During fuel cell operation, no new signals in the whole magnetic field range were detected for any of the membranes. It was expected that the Nafion membrane would show no traces of degradation due to its high stability, but for the two composite membranes no evidence of degradation processes was obtained either. Over the experimental

time range, the membranes were stable, and the steady concentration of organic radicals originating from the degradation processes probably was too low for detection by means of EPR. It should be noted that organic radicals originating from electron irradiation of polymer films have been detected at a level of a few times 10¹⁷ spins per gram [17]. They lead to characteristic structured spectra with a total width of frequently a few hundred Gauss.

5. Conclusion

We have built a miniature PEM fuel cell which runs in the microwave resonator of an EPR spectrometer. To our knowledge this is the first one world wide. It is shown that the cell leads to a strong signal which depends on the running condition. The signal originates from the electrode carbon material, and it is significantly altered by the presence of Pt catalyst particles. At this point, the detailed interpretation of the signal is open, but the changes during operation of the cell have been traced back to a reversible process that occurs in the presence of water.

Radicals originating from degradation have not yet been observed, probably due to sufficient membrane stability over the limited experimental time range and the soft running conditions. They will be in the focus of further studies.

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References

- [1] H. Wang, G.A. Capuano, *J. Electrochem. Soc.* 145 (1998) 780.
- [2] R. Hodgton, J.R. Boyack, A.B. LaConti, in: *Advance Development and Technical Report, No. 65DE5*, General Electric Co., West Lynn, MA, USA, 1966.
- [3] N. Aweir, *Eur. Polym. J.* 14 (1978) 9.
- [4] B. Sangchakr, T. Hisanaga, K. Tanaka, *J. Photochem. Photobiol. A: Chem.* 85 (1995) 187.
- [5] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, *Bull. Chem. Soc. Jpn.* 58 (1985) 2015.
- [6] F.N. Büchi, B. Gupta, O. Haas, G.G. Scherer, *J. Electrochim. Acta* 40 (1995) 3.
- [7] G.G. Scherer, *Polymer membranes for fuel cells*, *J. Phys. Chem.* 94 (1990) 1008.
- [8] D.M. Bernardi, M.W. Verbrugge, *J. Electrochem. Soc.* 139 (1992) 2477.
- [9] R.A. Assink, C. Arnold Jr, R.P. Holladsworth, *J. Membr. Sci.* 56 (1991) 143.
- [10] G. Hübner, E. Roduner, *J. Mater. Chem.* 9 (1999) 409.
- [11] D. Behar, J. Rabani, *J. Phys. Chem.* 92 (1988) 5288.
- [12] H. Kaczmarek, L.A. Linden, J.F. Rabek, *Polym. Degrad. Stab.* 47 (1995) 175.

- [13] J. Kerres, A. Ullrich, M. Hein, *J. Polym. Sci.* 39 (2001) 2874.
- [14] J. Kerres, *J. Membr. Sci.* 185 (2001) 3.
- [15] Q. Guo, P.N. Pintauro, H. Tang, S. O'Connor, *J. Membr. Sci.* 154 (1999) 175.
- [16] J.S. Wairright, J.T. Wang, D. Weng, R.F. Savinell, M.H. Litt, *J. Electrochem. Soc.* 143 (1996) 1233.
- [17] G. Hübner, Dissertation, Universität Stuttgart, 1999.
- [18] J. Kerres, W. Zhang, L. Jörissen, V. Gogel, *J. New Mater. Electrochem. Syst.* 5 (2002) 97.
- [19] L. Petrakis, G. Grandy, *Nature* 289 (1981) 476.
- [20] F.M. Bauman, Dissertation, Universität Stuttgart, 1998.
- [21] E.M. Cashell, V.J. McBrierty, *J. Mater. Sci.* 12 (1977) 2011.
- [22] M.S. Akther, A.R. Chughtai, D.M. Smith, *J. Appl. Spectrosc.* 39 (1985) 143.