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Critical size and surface effect of the hydrogen interaction of palladium clusters

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Abstract. Metal hydrides are used for electrochemical or gaseous storage of hydrogen because considerable amounts of hydrogen are reversibly absorbed and desorbed at interstitial sites. Palladium is often used as a model system. Nanophase material is of interest because properties related to the hydrogen absorption are size dependent. In this study, clusters from the size of 55 to 1415 atoms are investigated and compared with bulk Pd. It turns out that not only the amount of hydrogen per palladium that can be intercalated changes but also kinetics and chemical potentials are dependent on the cluster size. The clusters used for this study were chemically synthesised and stabilised by a ligand shell.

PACS. 61.43.Gt Powders, porous materials – 61.10.Nz Single-crystal and powder diffraction – 64.90.+b Other topics in equations of state, phase equilibria, and phase transitions dynamics

1 Introduction

The properties of clusters are of particular interest because they are often size dependent and different to bulk properties. Most of the studies in the literature were performed on clusters deposited on a substrate from evaporation sources [1,2] or with cluster beams in vacuum [3,4]. There are also chemical ways to obtain clusters. One is the electrochemical deposition on a substrate with current pulses [5,6]. A second method is the synthesis of clusters by reduction of metal ions in a solution and stabilisation with a ligand shell [7–10]. In all cases the two crucial problems are to separate the clusters to prevent them from further growth and to achieve size selectivity. The production of clusters and their properties such as ionisation potentials, photoelectron spectra, catalytic activity, shape or magnetic moment have been reviewed [11–14].

Metals, which form hydrides, can be used for hydrogen storage [15–17] and are interesting because properties such as conductivity or transparency [18] change with the hydrogen concentration. The hydride of bulk palladium has been extensively investigated [19,20] because the maximum hydrogen concentration is high for an elemental metal and it is noble. Nanocrystalline material was used to investigate the hydrogen palladium interaction of small grains. Mütschele and Kirchheim used compacted crystallites, which were obtained by solidification of metal vapour in a helium atmosphere [21,22]. Hydrogen was electrochemically incorporated in the sample. In a sample with a crystallite diameter of 8–12 nm an increase in the maximum α-phase concentration from 0.015 to 0.03 H/Pd was observed while the β-phase concentration decreased from 0.58 to 0.44 as compared to a polycrystalline sample with an average grain diameter of 20 μm. The measurement was performed at 333 K. They concluded that the grain boundaries that occupy 27% of the sample volume show an increased H solubility while they can not form to the β-phase because of their disordered structure. Natter *et al.* [23] used electrodeposited nanocrystalline palladium and hydrided the sample in the gas phase. They observed for a sample with an average grain diameter of 17 nm an α-phase composition of 0.04 and for the β-phase 0.45 at 318 K. In conformity with Mütschele and Kirchheim they attributed their results also to the grain boundaries which undergo no phase transition and therefore the sample has an increased maximum hydrogen solubility.

The increased solubility of hydrogen in the α-phase could clearly be attributed to the grain boundaries by Stuhr *et al.* [24]. At a low hydrogen concentration they found with neutron energy loss scattering two different hydrogen sites. Interstitial sites in the lattice and in the grain boundaries. The latter are occupied at a lower chemical potential and could therefore increase the α-phase solubility.

Eastman *et al.* [25–27] performed extensive X-ray diffraction and EXAFS studies on nanocrystalline palladium produced by gas condensation. The diffraction gave no evidence for the existence of large fraction of disordered grain boundaries. They hydrogenated samples while performing X-ray diffraction and showed that the whole sample transforms to the β-phase. The sample preparation

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Table 1. List of the properties of the samples used in this study. The percentage of surface atoms is given with respect to the total number of atoms.

Sample	Pd bulk	Pd^7	Pd^5	Pd^2
Diameter	63 μm	3.37 nm	2.5 nm	1.2 nm
Number of shells	—	7	5	2
Number of atoms	$\sim 10^{16}$	1415	561	55
Ligand	—	phenanthroline	phenanthroline	triphenylphosphine
Surface atoms	$\sim$ 0%	35%	45%	76%

used is comparable with the method used by Mütschele and Kirchheim [21,22] and it is remarkable that the results for the hydrogen concentration for the different phases match although different methods for hydrogenation were used. However, the results from Eastman are in contradiction to the conclusions of Mütschele and Kirchheim concerning the role of the grain boundaries. Eastman *et al.* point on the altered thermodynamic properties of the large amount of atoms in grain boundaries. The effect on the phase diagram is a narrowing of the miscibility gap.

Using Pd films a lowering of the critical temperature [28] has been found with decreasing thickness [29]. The critical temperature decreased from 560 K for bulk to 170 K for a Pd-film with a thickness of 6 nm on a glass substrate. When films are used the interaction with the substrate can not be neglected. This was shown in a study of palladium on gold [30], which revealed that no hydrogen could be absorbed in films with a thickness below 3 monolayers. Very small supported clusters were investigated by Tateishi *et al.* [31,32] who evaporated palladium on carbon. He found an almost bulk like capacity for clusters with a diameter above 3.1 nm and a dramatic decrease to 0.1 H/Pd for clusters with diameters of about 2 nm. On the other hand, clusters consisting only of up to 20 atoms investigated in a cluster jet by Fayet [33] could adsorb up to 3 deuterium atoms per palladium atom.

Monte-Carlo calculations [34] of a cluster consisting of 500 atoms and a radius of 1.3 nm predicted an increased capacity of 1.3 H/Pd. At low chemical potential the surface sites are occupied first with a subsequent filling of the interior sites. The calculations predict the disappearance of the phase transition.

Extensive studies on nanocrystalline palladium have been reported while little is known about clusters with diameters in the size range from 1 to 4 nm. This size region is of particular interest because the percentage of surface atoms varies from about 30% to 75% as shown in Figure 1. In the present paper we report about the results of electrochemical, gas phase and X-ray diffraction measurements on ligand stabilised clusters. These clusters can be produced with a very narrow size distribution [7,9] and in large amounts. The handling is very easy because they are stable in air. The crystal quality of the clusters is excellent as transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements revealed [9].

The narrow size distribution can be explained with the increased stability of closed shell clusters [11,35]. These closed shell clusters consist of "magic numbers" of atoms that are for cuboctahedra: 13, 55, 147, 309 for 1, 2, 3 and 4 filled shells, respectively. In this study clusters with 2, 5 and 7 shells (further called Pd^2, Pd^5 and Pd^7, which corresponds to 55, 561 and 1415 atoms) were used as listed in Table 1. The percentages of surface atoms with respect to the total number of atoms and the diameters of the samples are shown in Figure 1.

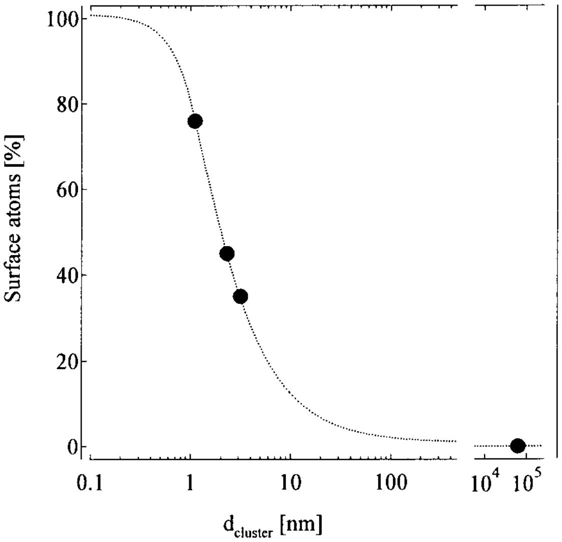

Fig. 1. The percentage of surface atoms changes with the cluster diameter. The samples used in this study are marked (●).

2 Experimental

The clusters are synthesised by reducing Pd ions from palladiumacetate with gaseous hydrogen in a aqueous solution. After reduction the Pd atoms start to form clusters. The final size of the clusters is a function of the reaction conditions such as temperature, ligand type and concentration. Drying the solution results in a powder of clusters. The size distribution is very narrow and centered around the magic numbers [7–9]

For the electrochemical measurements electrodes were produced. The cluster powder mixed with copper (Merck *p.a.* < 63 μm) or gold (Goodfellow *p.a.* < 63 μm) as compacting additive was pressed (500 MPa) to pellets. The powder stabilises the pellet (∅ = 7 mm) mechanically and still has enough porosity [36]. The mixing ratio between the compacting additive and cluster powder was 4:1 by weight. The pellets with bulk Pd (Merck *p.a.* $< 50\ \mu$m) were produced in a similar procedure. All hydrogen concentrations are refered to the mass of palladium neglecting the mass of the compacting additive and of the ligand shell.

The measurements were performed in a half-cell in 6 M KOH. Potentials were measured *versus* a Hg/HgO standard reference electrode. A nickel plate was used as counter electrode. Normal charge/discharge cycles were performed at currents of 25 mAh/g. The cut-off potential for discharge was -0.6 V *vs.* Hg/HgO. All hydrogen concentrations are determined from the amount of discharged current.

The equilibrium curves are measured in a pulsed mode. This means that the charge and the discharge cycle is divided in 50 pulses of a current of 10 mA/g. Each pulse is followed by a pause in order to equilibrate the electrode. This measurement leads to the equilibrium potential as a function of the hydrogen concentration in the sample. From the amount of discharge current at a certain potential one can determine the density of states for hydrogen at this potential.

The kinetic behaviour is tested in a special cycle where different discharge currents (range: 0.44 to 4400 mA/g) are applied and the resulting capacity is measured. Because of the reaction resistance higher currents lead to higher overpotentials and the cut-off potential is reached earlier, which results in a lower measured capacity.

The electrochemical measurements were performed to gain information about the amount of hydrogen, which can be stored in a cluster and about the kinetic and the (electro-) chemical potential of the reaction.

Gas phase measurements with as-produced cluster powder were done to exclude matrix effects from the compacting additive. A flow-controlled set up was used. The hydrogen concentration was calculated from the amount of desorbed gas.

All experiments, either gas phase or electrochemical were carried out at room temperature. The X-ray diffraction (XRD) measurements were performed with CuK_α radiation of a wavelength of 1.540 Å. The samples used for the diffraction were as-produced cluster powder before and after 10 cycles of hydrogen absorption and desorption from the gas phase. The absorption from the gas phase is advantageous for subsequent XRD because the cluster powder can be used in its original state.

3 Results and discussion

Table 2 lists the electrochemically measured maximum hydrogen capacity of three cluster samples compared with bulk palladium. The capacity decreases continuously with decreasing cluster size. The sorption of hydrogen in the clusters is a highly reversible reaction as shown in Figure 2 for Pd^5. During the first cycles the capacity increases and reaches a stable value for a large number of cycles. This behaviour is well-known from metal hydrides. Some activation cycles are necessary to remove surface impurities (*e.g.* oxygen) which hinder the hydrogen absorption. It is known [7,8] that the surface of the clusters that is not covered by the ligands is partly oxidised after the synthesis. From the cycle stability one can conclude that after the removal of the impurities the clusters do not decay upon the reaction.

Table 2. The measured maximum capacities in mAh/g and in the ration of hydrogen to palladium

Sample	Pb bulk	Pd^7	Pd^5	Pd2
Max. Capacity [mAh/G]	176	143	128	101
Max. H/M ratio	0.70	0.57	0.51	0.40

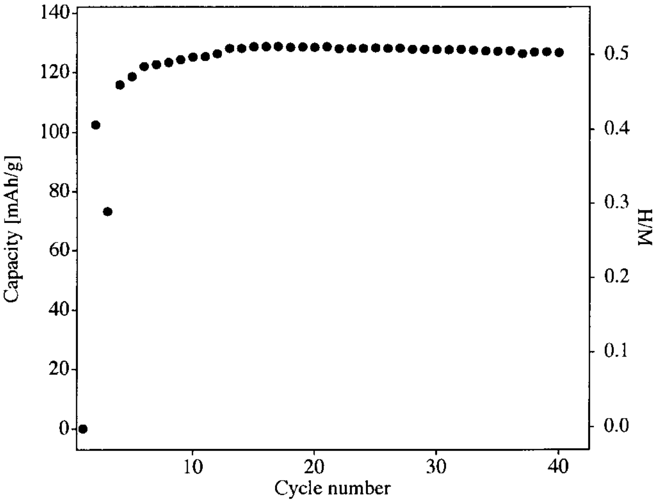

Fig. 2. The evolution of the hydrogen capacity as function of the number of charge/discharge cycles for 5-shell Pd-clusters. Several cycles are needed to activate the sample. Afterwards the capacity is stable. This shows the reversibility of the reaction.

The formation of bulk palladium hydride is characterised by a phase transition. At a low hydrogen pressure over the sample only small amounts of hydrogen are dissolved in the metal lattice, which is called the α-phase. At a high pressure the β-phase is formed. The transformation happens at about 20 mbar at room temperature. The same happens in an electrochemical experiment, where the applied potential corresponds to the hydrogen pressure. With increasing (electro-)chemical potential some hydrogen can be dissolved in the α-phase until the potential for the formation of the β-phase is reached. At this potential a large amount of hydrogen is absorbed as more and more of the palladium undergoes the phase transition. The hydride phase of Pd is still a *fcc* structure with an expanded lattice constant. This phase transition leads to a plateau in the equilibrium curves, which can be seen for bulk palladium in Figure 3. When the transition is completed one has to increase again the potential to dissolve further hydrogen. During an absorption/desorption cycle

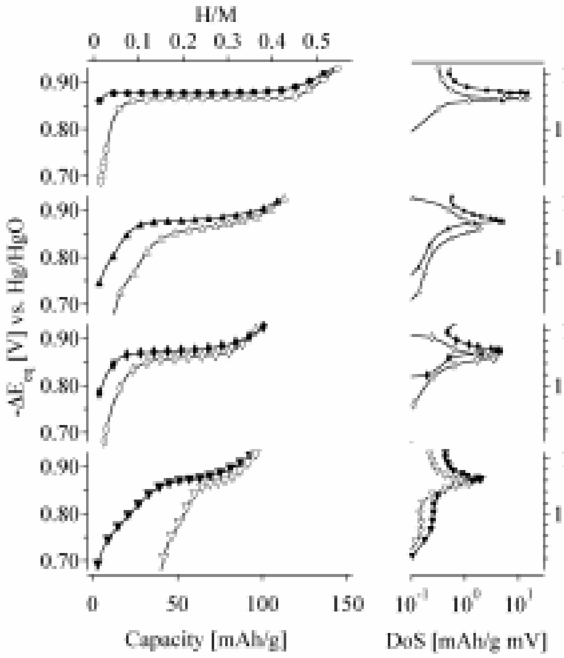

Fig. 3. On the left hand side the electrochemical potential as a function of hydrogen concentration is shown for bulk Pd (● charge; ○ discharge), Pd^7 (▲; △), Pd^5 (◆; ◇), and Pd^2 (▼; ▽). On the right hand side the density of hydrogen states as function of the electrochemical potential is plotted. The right axis shows the corresponding hydrogen pressure.

some energy is dissipated which can be seen as hysteresis in the equilibrium plot. On the right hand side of Figure 3 the density of hydrogen states versus the electrochemical potential is plotted. For bulk palladium there are sharp peaks at the potential where the phase transition occurs.

Figure 3 shows the decreasing width of the plateau with decreasing cluster size. There is still a clear plateau visible for Pd^5 and Pd^7, which proofs that the clusters do undergo the phase transition. But the DOS peaks broaden with decreasing cluster size. Surface and the subsurface shells of clusters are subjected to a relaxation [37,38]. A relaxation leads to an inequivalency of the hydrogen sites, which are located in these shells. This effect explains the tilt of the plateau and the broadening of the DOS peaks. Due to the negligible amount of surface atoms this effect is not observed in bulk samples.

In the case of Pd^2 it is not obvious from the equilibrium plot if there is still a phase transition. As already mentioned the critical temperature can be lowered. If the critical temperature is below room temperature a phase transition is no longer observed. For Pd films on glass the critical temperature is in the range of room temperature at a thickness of 55 nm [29].

The hydrogen pressure and the electrochemical potential is related by the following equation:

$$RT \ln\left(\frac{p_{\mathrm{eq}}}{p_0}\right) = -nF\Delta E. \tag{1}$$

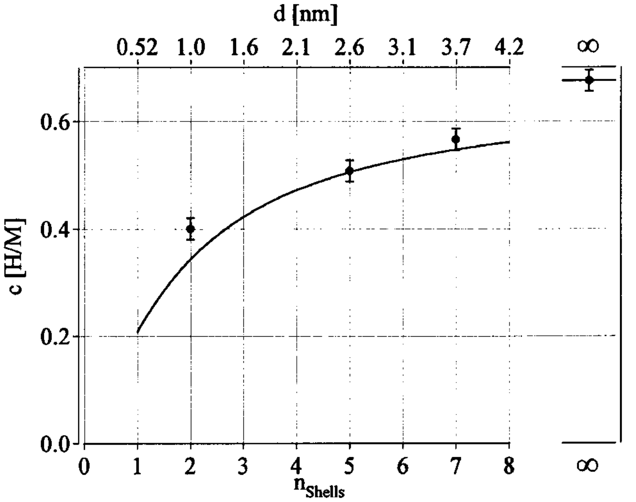

Fig. 4. The line shows the calculated decrease in capacity with decreasing cluster size. The markers show the measured capacities with their error bars.

p_{eq} is the equilibrium pressure and ΔE the electrochemical standard potential. For comparison the right axis in Figure 3 is labelled with calculated pressure units.

Theoretical calculations by Lee for a Pd cluster with 500 atoms [34] predicted the absence of a phase transition and an increased capacity of about 1.27 H/Pd. We compare this with the 5-shell cluster, which has about the same number of atoms. The capacity calculated is more than two times higher than the capacity we measured. Lee attributes the increased capacity to loading of hydrogen on surface sites. He found an equal number of hydrogen atoms stored on the surface and in the interior for a cluster of this size. The surface sites are occupied at a very low pressure. The predicted disappearance of the plateau that corresponds to an inability to undergo the phase transition is not in accordance to our data.

The narrowing of the plateau can be explained by the relative number of interstitial places, which decreases with decreasing cluster size. An atom on a face provides only 50% because it is half outside. In bulk palladium the hydrogen is incorporated in octahedral sites. The maximum H/Pd ratio of bulk palladium hydride is about 0.7 at room temperature. Therefore, only 70% of the sites can be occupied. Assuming that this ratio holds for the clusters and by counting the number of interstitial sites one can calculate the behaviour of the capacity for different cluster sizes as shown in Figure 4. The resulting capacity for interstitial sites has been calculated using a cuboctahedral structure. This structure has been confirmed by TEM, extended X-ray absorption fine structure (EXAFS) [13] and XRD [8] measurements. Lee predicted that most of the surface sites are occupied at a potential above −0.6 V *vs.* Hg/HgO. The adsorption energy for hydrogen on the surface of 102 kJ/mol for the (110) surface and 88 kJ/mol for (111) is much higher than for absorption in the bulk: 38 kJ/mol [39]. A potential above −0.6 V *vs.* Hg/HgO is not accessible when copper is used as compacting

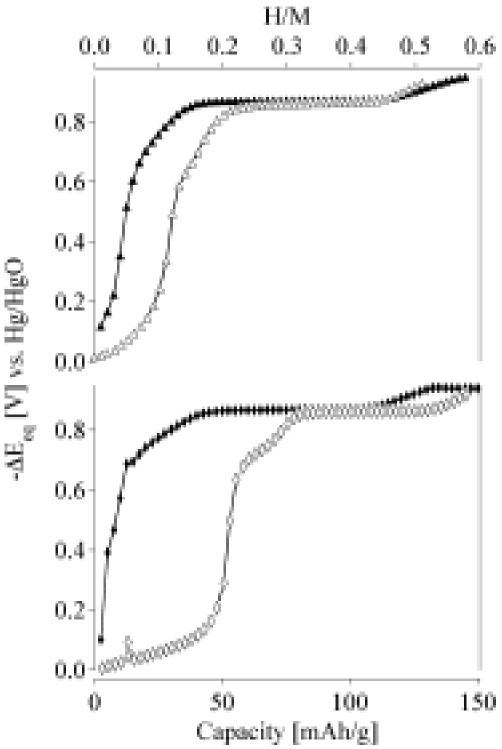

Fig. 5. Equilibrium curves of Pd 5-shell (♦; ◊) and Pd 7-shell (▲; △) clusters. The electrode has been prepared with gold as compacting additive to allow discharge to potentials up to 0.0 V *vs.* Hg/HgO. The hydrogen desorption from the surface occurs at much higher potentials than desorption from bulk sites.

additive because it would be oxidised. To avoid this the copper as compacting additive for electrodes was replaced by gold. Figure 5 shows equilibrium curves for Pd^7 and Pd^5 clusters where the cut-off discharge potential was set to 0.0 V *vs.* Hg/HgO. The plateau region at about −0.85 V *vs.* Hg/HgO remains unmodified. The potential and the width are independent of the compacting additive. There is a second hydrogen desorption between −0.2 and 0.0 V *vs.* Hg/HgO. The amount of desorbed hydrogen in this region is higher for the Pd^5 clusters. This can be explained by the larger surface that a smaller clusters possess. Using the known mean cluster size and the geometrical structure mentioned above one could calculate the number of hydrogen atoms adsorbed per Pd atom on the surface: the value is 0.48 for Pd^7 and 0.58 for Pd^5. This is below the coverage one would expect [39]. Due to the small size of the cluster a high percentage of the surface atoms are sitting on edges or corners (Pd^5 43%, Pd^7 31% of the surface atoms) providing less surface sites for hydrogen. Further some of the surface atoms are blocked due to the ligands (Pd^5 14%, Pd^7 12% of the surface atoms). Both together explain the relatively low coverage of the surface.

Using equation (1) one can compare gas phase with electrochemical measurements. To rule out any influence by the way of electrode production we used as-prepared cluster powder for gas phase experiments. The resulting capacity and plateau pressures match the values from electrochemical measurements.

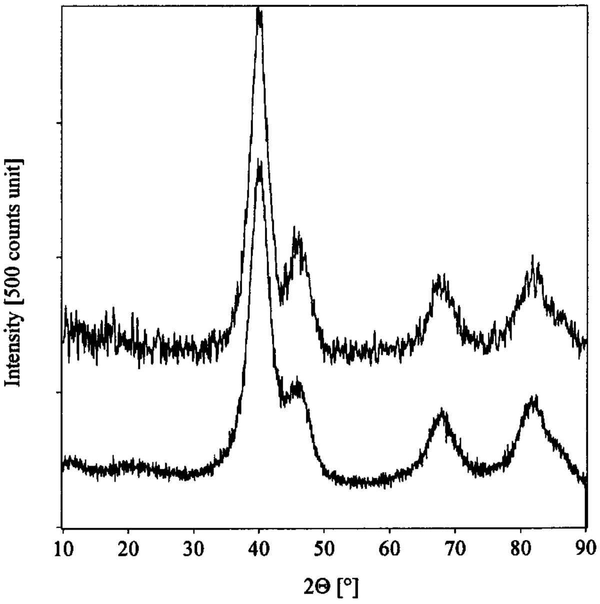

Fig. 6. X-ray diffraction spectra of the 7-shell clusters before (lower pattern) and after (upper pattern) several cycles of hydrogen absorption and desorption from the gas phase. The increased noise in the upper spectrum is due to a smaller amount of clusters used.

The gas phase experiment was also done to perform X-ray powder diffraction before and after several cycles of absorption and desorption. The results are shown in Figure 6. In both spectra the 111, 200, 220, 311 and 222 diffraction lines appear at the same positions as for bulk Pd. The width of the peaks is a measure for the mean grain size. One can see that the structure of the sample is not affected by cycling because the spectrum remains unchanged.

The kinetic properties of nanophase materials are improved. The percentage of full capacity (which was measured at a very slow discharge) as a function of discharge time is shown in Figure 7. One can see that bulk Pd (grain size 50 μm) has a very bad kinetic behaviour. To use reasonable amounts of the full capacity discharge times of several hours are necessary while all of the cluster exhibit reasonable discharge capacities when the discharge is in the range of minutes. The kinetics of palladium can be improved by two orders of magnitude with nanophase material.

4 Conclusions

The properties related to hydrogen absorption of palladium clusters such as capacity, equilibrium potential or kinetics vary with their size. We showed that the width of the plateau decreases with decreasing cluster size. This is due to the reduced number of interstitials. The plateau is more and more tilted with decreasing cluster size,

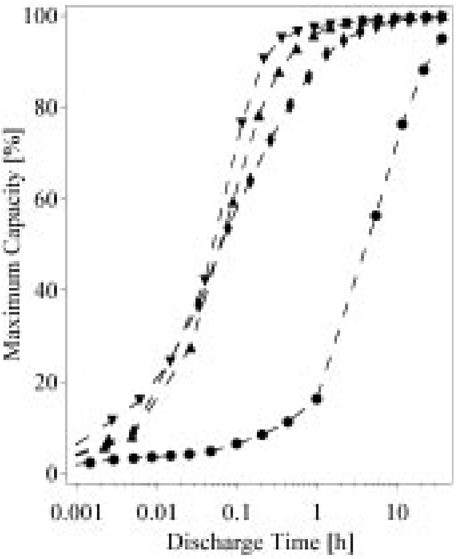

Fig. 7. The discharge capacity is due to the reaction resistance a function of discharge current. This plot shows the percentage of the discharge capacity at different discharge times for bulk Pd (●), Pd^7 (▲), Pd^5 (⧫) and Pd^2(▼).

which can be explained by the relaxation close to the surface. However, the Pd^5 clusters show a plateau unlike theoretically predicted. Even clusters of a diameter of 1.2 nm show a reversible hydrogen uptake.

There is a reversible adsorption of hydrogen on the surface. Due to the small percentage of surface we did not observe this effect for bulk Pd but for Pd^5 and Pd^7. The cluster samples show a dramatic improvement in discharge kinetics compared to bulk. X-ray diffraction revealed that the crystallographic structure of the clusters is not altered by absorption/desorption cycles.

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