10 Summary

In this work the scanning flow cell (SFC) was successfully applied for the comprehensive characterization of electrocatalysts utilized in fuel cells for the oxygen reduction reaction (ORR). To approach this task the SFC was improved substantially to enable catalyst research under controlled conditions. The cell geometry was adapted towards a controlled, reproducible and flexible V-shaped design. Theoretical calculations support the defined mass transport and the reliability of the system. An important step was the implementation of a gas purging system with an automated gas exchange, the optimized adjustment of gas and electrolyte transportation, as well as the implementation of an external purging as a key feature to enable measurements free of external influences from the surrounding air. An ICP-MS has been utilized as an analytical tool to detect the dissolution of different species from the catalyst during the electrochemical treatment. In order to enable the characterization of high-surface area catalysts (HSAC), a Nano-Plotter™ was utilized to print locally defined layers of catalyst material onto a carbon plate. The homogeneity of the layers was improved to obtain consistent results, while the determination of the exact loading of catalyst, i.e. the amount of deposited material, still requires further investigations. Although less catalyst than expected is deposited during the printing process, dissolution experiments showed that the trends within one printed pattern are reliable and the electrochemical determination of the real surface area of the catalysts is an accurate descriptor to normalize the dissolved amounts and make different experiments comparable. Especially the initial qualitative trends determined from the presented studies have confirmed the high reliability of the approach.

The applicability of the modified SFC was validated on polycrystalline, bulk Pt as a model system for the ORR. In the course of the validation it was proved that the geometric and the real surface area can be determined accurately, and the same analytical methods as in classical electrochemical setups like the rotating disc electrode (RDE) can be utilized. Based on the complete gas saturation and air shielding, reproducible CVs in inert as well as in oxygen saturated electrolyte can be obtained, and the expected electrochemical features of Pt are perfectly reproduced. The determined specific activity is lower than the highest reported literature value, but as the deviation can be expected to be systematic, trends in the activity can be detected sufficiently accurate, as proven by the subsequent measurements. The possible influence of impurities on the measurements was discussed, but is expected to be low for potentiodynamic measurements, especially if adsorbed molecules are regularly stripped from the surface at high potentials.

The validated setup was then utilized for an intense study of Pt-Cu alloys of a thin-film material library. The characterization of the sample with various physical methods revealed a continuous composition gradient. The composition of 19 electrochemical measurement locations were determined specifically with XPS. Within the micrometer scale a homogeneous material distribution is present, although the grains have a slightly preferred surface orientation in the (111) direction. The different alloys on the material library were screened concerning their composition-dependent properties, for which a fixed potential protocol with constant potential limits was applied on each measurement location. For low Cu concentrations up to 25 at% Cu, stressful cycling up to 1.6 V_RHE leads to a Cu dissolution that progresses approximately 4 MLs into the alloy. For higher Cu contents the dissolution depth slightly increases up to 8 MLs until a composition of 57 at% Cu, where
massive dissolution under the formation of a porous structure with pore diameters of 3 – 10nm occurs. This defines the parting limit of the Pt-Cu system, which lies slightly below 57at%Cu. In parallel, the activities of the alloys were analyzed and an initial increase up to an enhancement factor of 2.2 versus the specific activity of polycrystalline Pt was found. However, within the given accuracy no further increase in specific activity could be detected for compositions above 20at%Cu. When taking the decrease of the amount of Pt in the alloy into account, the activity per utilized Pt keeps increasing with the Cu content. Even above the parting limit the enhancement factor for the alloy is not higher, yet even decreases with continuous porosity formation.

For a few selected compositions more detailed potential-dependent studies were conducted to elucidate the dissolution mechanism. Small Cu dissolution already sets in at 0.35V_{RHE} for all compositions, which is however only detectable in very slow potential sweeps. More significant dissolution occurs around 0.9V_{RHE}, which coincides with the onset of oxide formation on Pt. This leads to a restructuring of the surface and certainly influences the mobility and the binding energies of the atoms at the surface. With further increasing potential the dissolved amounts during a full CV increase, while if the potential is just slowly increased above this potential the dissolution rate drops to a constant level and afterwards follows the behavior of the Pt dissolution. This is a first indication that the Cu dissolution is significantly linked to the transient behavior of the Pt dissolution mechanism. Within a single CV Cu dissolves mainly during the anodic sweep, while Pt follows the same dissolution behavior as in a pure Pt electrode and mainly dissolves during the reduction of the surface in the cathodic sweep. In spite of this apparent contrast in the extent of the respective dissolution, the dissolution processes are nevertheless strongly correlated. This was proven by the linkage of the dissolved amount during multiple as well as during single cycles, as for example a dissolution of Cu during the cathodic sweep can only be detected when Pt dissolves anodically. Note that the amounts do however not match each other stoichiometrically, but rather for one dissolved Pt atom significantly more Cu atoms dissolve. With ongoing depletion of Cu from surface-near regions this factor naturally decreases, which brings in a strong time dependent factor. For alloys above the parting limit these statements are also valid, but for potentials above the critical potential the passivation of the surface with Pt breaks down leading to the above mentioned porosity formation. For the investigated composition of 57at%Cu this potential is above the dissolution potential of Pt. As Pt preferentially shows a transient dissolution behavior under the experimental conditions, in contrast to the dominating steady-state dissolution on e.g. Au, the classical dealloying theory is not fully applicable for this case. According to kinetic considerations, a correlation of the critical potential with the oxide formation on the Pt surface could be expected, but as the critical potentials for alloys with higher Cu content are reported to be below the onset for oxide formation, a mainly thermodynamically driven process is more likely.

The influence of the composition as a parameter for the performance of a catalyst was characterized with the study on the Pt-Cu alloy thin-film material library. In a second step the influence of the morphology was investigated. For this purpose four standard Pt HSACs with different particle sizes were analyzed. The trends in activity already found earlier in RDE studies on the same catalysts were reproduced. Namely a particle size independent specific activity for particles with a diameter ≤ 5nm, and a higher activity for larger, but also unsupported nanoparticles almost close to the activity of bulk Pt was found. The combinatorial approach of the SFC/ICP-MS
system additionally allows the investigation of the stability of these catalysts towards dissolution. The preliminary results of this study indicate that especially very small particles with a diameter $\leq 1\,\text{nm}$ are more sensitive to dissolution and the dissolved amounts per cycle are almost doubled in comparison to the larger particles, for which the dissolution rates per Pt surface area are comparable to that of bulk Pt. In contrast to theoretical predictions, no shift of the onset potential was found. Also, the mass CVs of the HSACs show the same shape as for bulk, polycrystalline Pt, indicating that the dissolution mechanisms remain the same even for the decreased system size.

Finally, the parameters of morphology and composition were combined in the analysis of a PtNi HSAC. The analyzed particles have a size distribution between 3 and 7 nm, above the limits for increased dissolution as found for pure Pt catalysts. The dissolved amounts are compared to a Pt$_3$Ni bulk material. As the results on Pt-Cu thin-film alloys indicate, the composition can be quite an important factor for the dissolution properties, but within the timeframe of this work no extensive study on the composition-dependent behavior of Pt-alloy HSACs could be conducted. Therefore the results are compared among the given materials under consideration of the different stochiometries. These initial results indicate that the Ni dissolution is significantly enhanced in the nanoparticulate sample in comparison to the bulk alloy. However, in a potential-dependent study no change in the onset potentials for neither Ni nor Pt could be found, in agreement with the previous results. Similar to Cu, Ni dissolves mainly anodically, and no distinguished Ni dissolution during the strong cathodic Pt dissolution could be detected.

In summary, the SFC has been successfully applied for catalyst research and new, highly valuable insights into the ORR reaction and dissolution processes have been obtained. Especially in combination with downstream analytics by the ICP-MS the dissolution behavior of various materials have been resolved. The screening ability and the high reproducibility of the results open up a huge range of systematic studies on various parameters that influence the catalysts properties, so that the SFC will continue to provide valuable information on electrochemical systems in future. Already the obtained results of this thesis indicate clear trends that are important for the rational design of future catalysts, as they define stability windows and describe potentials and limits for a possible activity gain.