

Abstract

Within this thesis the reaction mechanism of the MCFC cathode reaction was examined and searched for a way for its acceleration. This mechanism has been a subject of research activities since 40 years. Exceeding the pure scientific interest the knowledge about this mechanism and conclusions for lowering the MCFC operation temperature can play a key role in commercialisation of an efficient heat&power cogeneration system. Conclusion of this thesis findings were included in the EUROcell design, a new concept for MCFC electrodes, cells and stack components. The performance of the EUROcell cathode significantly exceeded those of state of the art cathodes. AC impedance studies confirmed that the design change resulted in the acceleration of that process, that should be influenced by the variations.

Due to the aggressive carbonate melts and high melting points electrochemical examinations turned out to have high requirements to the experimental setup. Particularly investigations on oxygen reduction suffered from low concentrations of the electroactive species and thermal signal broadening. Still there is no consensus in literature about the nature of dissolved reducible oxygen species inside the electrolyte melt. For reasons of this experiments were performed under atmospheric MCFC gas conditions using fast cyclic voltammetry for obtaining acceptable signals in spite of low concentrations inside the eutectic lithium-potassium carbonate melt. The scanrate was varied between 1 V/s and 10.000 V/s whereas the higher scanrates may have led to irreversible conditions, so a direct comparison to signals obtained by adding per- or superoxide was not possible. The signals of added per- and superoxide ions appeared to be identical with a one electron transfer during the rate limiting step. As a hypothesis this step was attributed to the reduction of superoxide to peroxide ions.

The electrochemical behaviour of various metal oxides (Sb, Cr, Bi, Cu) was examined during a screening for a homogeneous redox catalyst (mediator) for the charge transfer reaction. By using cyclic voltammetry copper ions were found to show a change from oxidation state I to II in the potential range of a MCFC cathode, fulfilling a necessary requirement on a mediator. Each of the tested metal compounds is converted to the metallic or an insoluble state within the potential range of a MCFC so that a solid deposition inside the matrix or anode would occur during long term operation. Surprisingly there was no effect on the cell performance observed within a lab-scale cell test using a copper oxide redox catalyst activated cathode though a meditative action for the charge transfer should take place.

During impedance investigations on the cathode reaction in a 250 cm² laboratory cell an artefact of the cell internal reference electrode was found which makes a reliable evaluation of the spectra more difficult or even prevents it. To undergo this artefact a symmetrical cathode half cell testbed was developed which allowed mechanistic studies and tests independent of reference electrodes. In this testbed a large range of cathodes were examined with changes of the significant cathode parameters such as temperature, partial pressures, current density, materials, morphologies and different degrees of electrolyte fillings.

Through variation of the electrolyte filling level it was possible to separate the polarisation processes by their time constants. The different processes were examined with regard to reaction orders as well as dependencies of temperature and current density. These impedance elements were assigned to physical and chemical processes by use of plausible values of expectation, significance, reaction orders, activation energies and long term observations. The reaction model so obtained does not show any significant impedance contribution of the charge transfer resistance but an important role of gas transportation limitations, a slow start reaction (formation of reduceable electrolyte-soluble oxygen species) as well as a slow recombination of oxide ions and carbon dioxide.

In accordance with models found in literature the cathode reaction is mainly limited by transport processes in the high temperature range of about 650°C whereas in the range of 550°C a cinetical limitation is dominant. This reaction model was transferred to a complete equivalent circuit of the MCFC cathode by assigning the obtained processes to adequate partial equivalent circuits. Combining the examined processes and with their predicted dependencies based on values of expectation for basic operation parameters a mathematical formulation of the corresponding impedance elements / cathode behaviour was obtained. The simulated cathode impedance spectra and dependencies based on these results are in good accordance with experimental results.

The reaction model leads to some conclusions how MCFC cathodes could be improved. These conclusions were taken into consideration during the design of a new cathode type for the Eurocell concept. The cathode showing high impedance due to poor gas transport was divided into two functional separated layers, one optimised for the electrochemical reaction and the other one improved for gas transport properties using a macroporous structure. Laboratory cell tests using this cathode type allowed to lower the operation temperature to 600 °C and improved power density.

Until now there are some important effects not included in the model such as thermochemical effects on electrolyte distribution, moisture influences and effects of the anode side. In earlier literature steam is considered as an inert gas in the cathode reaction. A lab cell test with cathode gas humidity corresponded to system conditions showed a significant influence of the water partial pressure on the overall power output and cathode polarisation. The mechanism behind this interaction still is unclear; it is considered to a different electrolyte basicity and / or different electrolyte contact angles in dry and humid atmosphere. In the further development this effect could prove to be valuable for improved power density of a MCFC. An increased power density and lifetime are the key parameters in commercialisation of MCFC systems as a clean and efficient heat and power co-generation technology.