

Influence of carbonate ions and temperature on the oxygen reduction reaction at platinum in alkaline media
 C. Cremers, B. Kintzel, K. Pinkwart, J. Tübke
 Fraunhofer Institute for Chemical Technology ICT
 Department for Applied Electrochemistry
 Joseph-von-Fraunhofer-str. 7, 76327 Pfinztal, Germany

A number of existing and emerging electrochemical power sources like fuel cells and metal air batteries use air electrodes as cathode to deliver electrical energy. In an acidic environment like in a proton exchange membrane fuel cell, the oxygen reduction reaction at platinum electrodes, which are most commonly used, is known to exhibit large over potentials. These over potentials reduce the efficiency of the power sources and their reduction is therefore of high interest. One approach to achieve this goal might be to change the pH in the electrode from acidic to alkaline. This has become of more interest with the introduction of new alkaline anion exchange membrane electrolytes which avoid some of the drawbacks of liquid bases. However, the effect of carbonate on such electrodes is still not entirely clear. E.g. Vega and Mustain report a reduction of the ORR activity of platinum in presence of carbonate ions but also a slight increase of performance of an actual fuel cell in carbonated state [1]. This increase in performance is in agreement with other literature reports [2,3] but not with the finding of reduced ORR activity [1] and increased membrane resistance [4].

In order to further investigate this issue test experiments were performed the ORR activity of a polycrystalline platinum disk electrode was measured as function of the concentration of carbonate ions in the electrolyte and of the temperature. In order to simulate the saturation of the vase by carbon dioxide the carbonated electrolytes were prepared in such a way that the concentration of the cation was kept constant by replacing two parts of KOH by one part of K_2CO_3 . The measurements were performed with a Pine RDE set-up in a double walled cell using a reversible hydrogen electrode by Gaskatel as reference electrode and platinum gauze as counter electrode. By an external thermostat the temperature of the cell was varied between 20 °C and 60 °C. In addition measurements in sulfuric acid solution were performed for comparison. For the measurements the rotation speed was varied between 100 rpm and 2500 rpm. From the measured currents at the different rotation speed kinetic limiting current were determined using the Koutecky-Levich analysis method.

At a temperature close to the ambient temperature it was found that the ORR activity of the platinum electrode is strongly reduced with increasing carbonate concentration (cf. fig. 1). This is in agreement with the findings of [1]. In comparison two the ORR in the sulfuric acid solutions the kinetic current for the ORR in alkaline solutions is also found to be higher for potentials of 0.7 V or above except for the case of pure potassium carbonate electrolyte. However the kinetic currents at low potentials increase much stronger in the acidic environment. In principle this is also the case for the pure potassium carbonate solution, which with a pH of about 11 is more acidic than the other alkaline solutions.

The situation changes at a higher temperature of 50 °C. Here a strong increase of the activity of the electrode in the acidic environment is observed so that the kinetic currents in sulfuric acid solution at 0.7 V vs. RHE are

higher than those in alkaline solution. Also the current in pure carbonate solution is strongly increased so that kinetic currents are higher than in other alkaline solution at potentials of 0.6 V or lower.

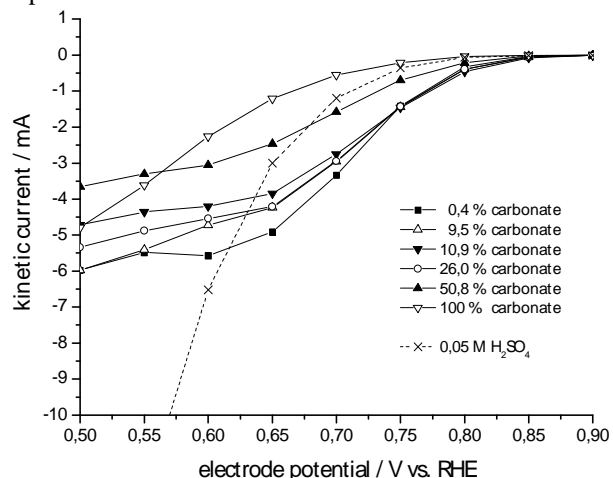


fig 1: Kinetic currents for the ORR at 20 °C at a platinum disk electrode in oxygen saturated electrolyte with varying carbonate concentrations.

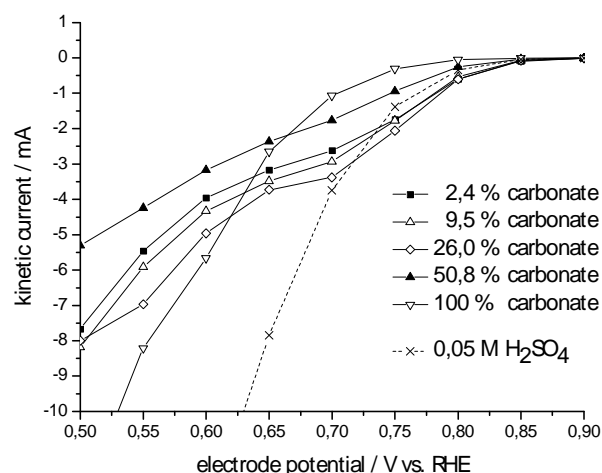


fig 2: Kinetic currents for the ORR at 50 °C at a platinum disk electrode in oxygen saturated electrolyte with varying carbonate concentrations.

As fuel cell test in contrast to most three electrode measurement are usually performed at higher temperature around 50 °C this may in part explain the difference found in literature. In the presentation details on the experimental results will be shown together with the results ongoing RRDE measurements investigating the H_2O_2 production as function of carbonate concentration and temperature

- [1] J.A. Vega, W.E. Mustain, *J. Power Sources* 195(21), 2010, pp. 7176 – 7180
- [2] L.A. Adams, S.D. Poyton, C. Tamain, R.C.T Slade, J.R. Varcoe. *ChemSusChem* 1(1-2) 2008, 79-81
- [3] M. Unlu, J. Zhou, P.A. Kohl, *Electrochem. Solid State Lett.* 12(3) 2009, B27-B30
- [4] M. Inaba, Y. Matsui, M Saito, A. Tasaka, K, Fukuta, S. Watanabe, H. Yanagi, *Electrochemistry* 79(5) 2011, 322-325