## Contents

1 Introduction ................................................................. 1

1 Oxygen reduction reaction .............................................. 3
   1.1 Introduction .......................................................... 3
   1.2 Current knowledge of ORR mechanism ........................... 3

2 Electrochemistry of metal and semiconductor electrodes ............ 7
   2.1 Introduction .......................................................... 7
   2.2 Metal electrode ....................................................... 7
   2.3 Semiconductor electrode .......................................... 10

3 Vibrational Spectroscopy ................................................. 13
   3.1 Introduction .......................................................... 13
   3.2 Vibrations of molecules ............................................ 13
   3.3 Infrared absorption spectroscopy in reflection geometry ....... 14
      3.3.1 Electric fields at interfaces for quantification of spectra 17
   3.4 Raman spectroscopy ............................................... 19
   3.5 Literature review of vibrational spectroscopy of intermediates of ORR 20

4 Experimental ............................................................... 23
   4.1 Sample preparation .................................................. 23
   4.2 Measurement and analysis of ATR-IR spectra ...................... 24
   4.3 Set-up for Raman study of decomposition of KO₂ ................ 25
4.4 Surface Characterization techniques
4.5 Chemicals

5 Spectroelectrochemical cell set-ups
5.1 Spectroelectrochemical cells
   5.1.1 Cell with stagnant electrolyte
   5.1.2 Continuous flow cell
5.2 Electrodes

6 ORR on Ge(100) in acidic solution
6.1 Introduction
6.2 CV of Ge(100) in acidic medium
6.3 ATR-IR spectra during ORR on Ge
6.4 ATR-IR spectra of isotope-labelled ($^{18}$O$_2$) experiment
6.5 Control experiments with stable reference compounds
6.6 DFT calculations of possible ORR intermediates
6.7 Spectral interpretation of ATR-IR spectra during ORR
6.8 Surface coverage of detected intermediates during ORR
6.9 Mechanism of the ORR in acidic solution
6.10 Summary

7 Potential-dependent transformation of the surface termination of
  Ge(100) and Ge(111)
7.1 Introduction
7.2 Analysis of the GeH mode at different pH
7.3 Ge(100) in HClO$_4$
7.4 Ge(111) in HClO$_4$
7.5 Surface morphology of Ge electrodes after experiments
7.6 Discussion
7.7 Summary