

Confirmation of Gas Loading Induced Defects by Complex Impedance Spectroscopy

TECHNICAL AREA:

The adsorption and absorption of gases into solid materials have been investigated for many applications including fuel cells, catalysis and low-energy nuclear reactions (LENR).

BACKGROUND:

The loading of hydrogen (or its isotopes) into a solid material is an important technology for hydrogen fuel cells and LENR. The loading of methane into metal-organic frameworks is an important, emerging technology to increase the storage capacity of this fuel source. The loading process must be controllable, quantifiable and sustainable to be repeatable and production-worthy.

EXISTING TECHNOLOGIES:

The primary technologies for measuring loading are mass change and pressure change (or some means of calculating the number of gas molecules which are no longer in the gas phase and therefore adsorbed on or absorbed into a solid sample). Changes in resistance are occasionally used after the resistance has been calibrated against mass change.

PROBLEMS WITH EXISTING TECHNOLOGIES:

For materials which are to be loaded and activated in a continuous process, neither mass change nor pressure change is practical. A scale cannot be implemented in a reactor. High accuracy pressure change analysis instrumentation is also very difficult to implement in a multipurpose system. The resistance measurements are either AC at a single frequency or DC. These resistance values cannot be correlated with their conduction paths.

SUMMARY OF THE PROPOSED SOLUTION AND THE ADVANTAGES THE PROPOSED SOLUTION PROVIDES:

Complex impedance spectroscopy probes an electrochemical system with a small AC-perturbation over a range of frequencies. It is a non-destructive method which enables measurement of the impedance of different conduction paths and conducting species in a material. After being calibrated with the presence of a desirable conduction path or species, complex impedance may be used as a confirmation or quality control tool.

DETAILED DESCRIPTIONS OF THE PROPOSED SOLUTION AND FIGURES:

The basics of complex impedance spectroscopy (CIS) are widely available. An introduction to the technique can be found here: <http://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/> among other places. Two aspects of CIS which are very important to its application for measurement of gas loading in solids are:

- 1. The measurement of impedance for both ionic and electronic conduction.*
- 2. The measurement of impedance to ions and electrons conducting along different paths.*

Many conduction paths exist in a crystal lattice. Among those paths, along the surface, along grain boundaries, through bulk grains and defect "hopping" are common. A crystal defect is defined as any irregularity in the crystal structure. Grain boundaries are defects since they represent a discontinuity between grains of continuous crystal structure. The term defect is more typically used to describe a missing atom in a crystal structure. Missing atoms represent openings in a crystal structure by which an ion could "hop" from one to another thereby conducting through a crystal.

CIS is able to access the various conduction paths in a crystal structure by AC perturbations over a large frequency range, typically from 1 Hz to at least 10 MHz. Figure 1 is a schematic of a simple crystal structure and Figure 2 is the expected complex impedance spectra of that structure. Electrodes may be placed on the opposite sides of a sample as suggested in Figure 1 or on the same side of a sample. Depending upon the size of a sample, having the electrodes on the same side may be advantageous for minimizing the physical distance of the surface conduction path. Note

as described above, different frequencies probe different conduction paths. Lower frequencies measure the impedance to conduction along the grain boundaries. Higher frequencies measure the impedance to conduction through the grains. The electric circuit model equivalent to the complex impedance spectra is shown in Figure 3. Crystalline solids typically fit a parallel capacitor and resistor circuit model. As shown in Figure 2, the resistance (R) of a conduction path can be taken from the lower frequency by taking the difference between the higher and lower intercepts of the semi-circular spectra with the real impedance (Z') axis. For example, assume that the intercepts along the Z' axis of a measured spectra are R_A , R_B and R_C as shown in Figure 4. The resistance value which most likely corresponds to the surface or grain boundary resistance is calculated by taking the difference between R_C and R_B . The resistance value which most likely corresponds to the bulk resistance of the crystalline grains is calculated by taking the difference between R_B and R_A .

The trapping or releasing of conducting species from a defect is affected by temperature, so it follows that both ionic and electronic conductivity are affected when crystal defects are present. The change in resistance as a function of temperature may be used to calculate activation energy of a defect as follows. So as not to introduce potential errors via changing sample or electrode dimensions, conductance (as opposed to conductivity) is calculated from Equation (1):

$$1/R = B \exp(-E_c/kT) \quad (1)$$

where R is resistance
 E_c is the activation energy of conductance (eV),
 k is Boltzmann's Constant = 8.1673×10^{-5} eV/K,
 T is the absolute temperature (K) and
 B is a constant.

A plot of $\ln(1/R)$ as a function of $1/T$ has a slope of $-E_c/k$ allowing calculation of E_c .

Initially, physical analysis of samples by methods such as scanning tunneling electron microscopy, will be required to match defects with conductivity. An alternative is to match an activation energy with an observed sample behavior through repeated experiment. This activation energy can then be used to confirm the presence of a

certain type of defect. Figure 5 is a flowchart for using CIS to confirm the presence of a defect.

Examples of types of defects and conductivities which could be of interest for LENR applications and therefore become embodiments or claims of the patent are:

1. *Electronic conduction along the grain boundaries in a defect free sample*
2. *Electronic conduction through the bulk grains in a defect free sample*
3. *Ionic conduction of hydrogen or deuterium ions along the grain boundaries in a defect free sample*
4. *Ionic conduction of hydrogen or deuterium ions through the bulk grains in defect free sample*
5. *The effects of the number of hydrogen or deuterium atoms loaded into a defect free lattice on electronic and ionic conduction*
6. *The effects of single atom or multi-atom defects on electronic and ionic conduction*
7. *The effects density / proximity of single atom or multi-atom defects (defect cluster) on electronic and ionic conduction*
8. *The effects of the number of hydrogen or deuterium atoms loaded into a multi-atom defect on electron and ionic conduction.*

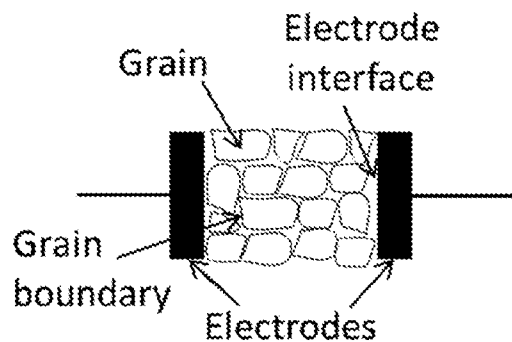
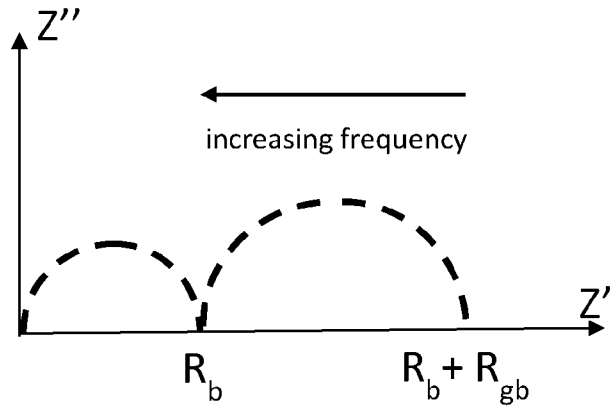


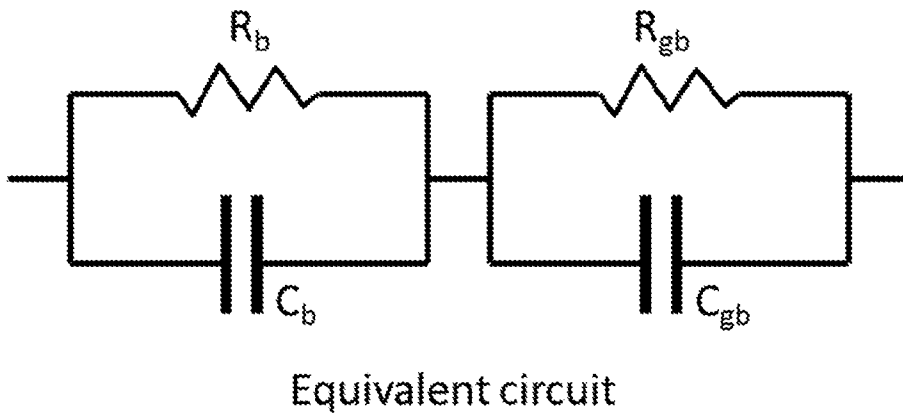
Figure 1



R_b = bulk grain resistance

R_{gb} = grain boundary resistance

Figure 2



R_b = bulk grain resistance
 C_b = bulk grain capacitance
 R_{gb} = grain boundary resistance
 C_{gb} = grain boundary capacitance

Figure 3

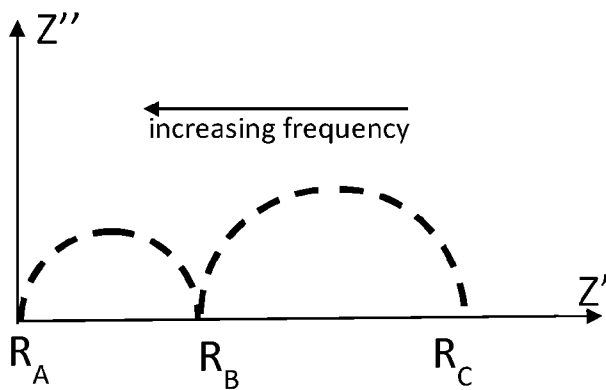


Figure 4