Induced polarization of carbon materials

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Introduction

Carbon materials exhibit more or less electronic conductivity and as a consequence they may show strong polarization effects when they are in contact with electrolytes and other less conductive materials, e.g. in supercapacitors or as biochar in soil. For an insulating mineral with a charged surface (e.g. sand), polarization is mainly due to a fast compression and dilatation of the diffuse electrical double layer and a slow movement of counterions in the Stern layer. Applying an electrical field to electronically conducting particles (e.g. graphite) induces a large dipole moment across the particle. This fast process is followed by a slow rearrangement of ions in the surrounding solution (Fig. 1). The time needed for the slow processes depends on the particle size. In contrast to ideal graphite, carbon materials made by pyrolysis from natural sources have functional groups and surface charges. Thus all mechanisms shown in Fig. 1 may influence their polarization. In addition, redox reactions taking place at the interface between the electronically conducting particles and the electrolyte or other solid material may lead to leakage currents that reduce the polarization. The goal of this work was to study the influence of the electronic conductivity, the particle size and the chemical composition of carbon materials on the induced polarization of their mixtures with a non-conducting material (sand) and an electrolyte.

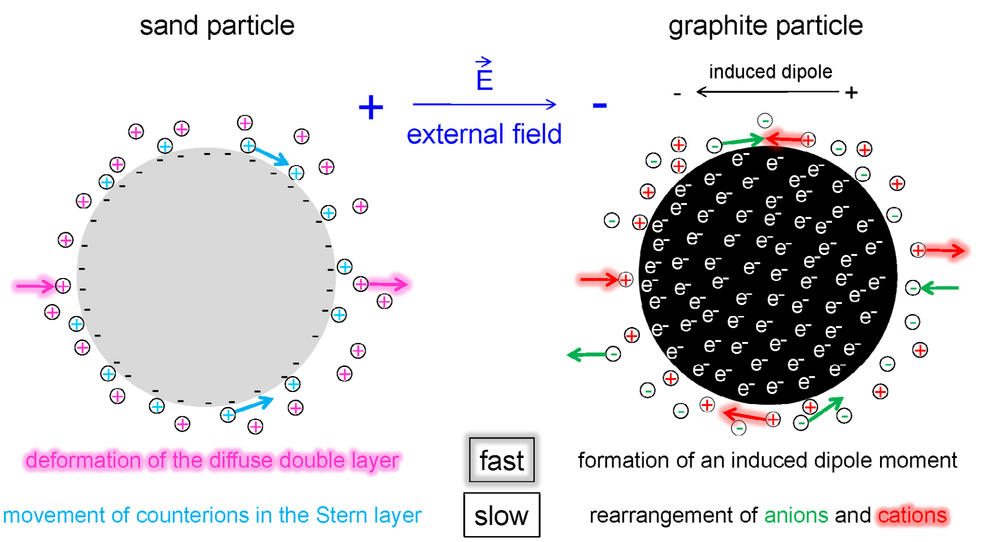

Fig. 1: Polarization mechanisms for sand particles and graphite particles.

Materials and methods

Series of commercial activated carbons with well-defined particle size and biochars made under different conditions were investigated. Sand with a particle size between 125 and 250 µm was used as non-conducting material.

The magnitude of the complex electrical conductivity $|\sigma^*|$ of some air-dry carbon materials and air-dry sand was determined in a two-electrode configuration between two bronze plates in the frequency range from 1 Hz to 45 kHz. The complex electrical conductivity $\sigma^* = \sigma' + i\sigma''$ of 2 % carbon in sand saturated with 4 mM NaCl was measured in the frequency range between 1 mHz and 45 kHz with an impedance spectrometer built at Forschungszentrum Jülich.

Results

The magnitude of the conductivity of carbon materials can vary over several orders of magnitude as shown in Fig. 2a. The conductivity of sand is ca. 10^{-8} S m^{-1} at 1 Hz and increases with frequency due to a capacitive current. This behaviour is typical for an insulator with a low leakage current. The conductivity of the charcoal with 1-2 mm size is somewhat larger, but still in the range of an insulator. The active carbons and the gasification coke show much higher conductivity in the range of semi-conductors and there is no significant capacitive current in the observed frequency range. The carbon materials with high conductivity show large polarization, but the charcoal with low conductivity also has a noteworthy polarization with a clear maximum of the imaginary part of the complex conductivity (Fig. 2b).

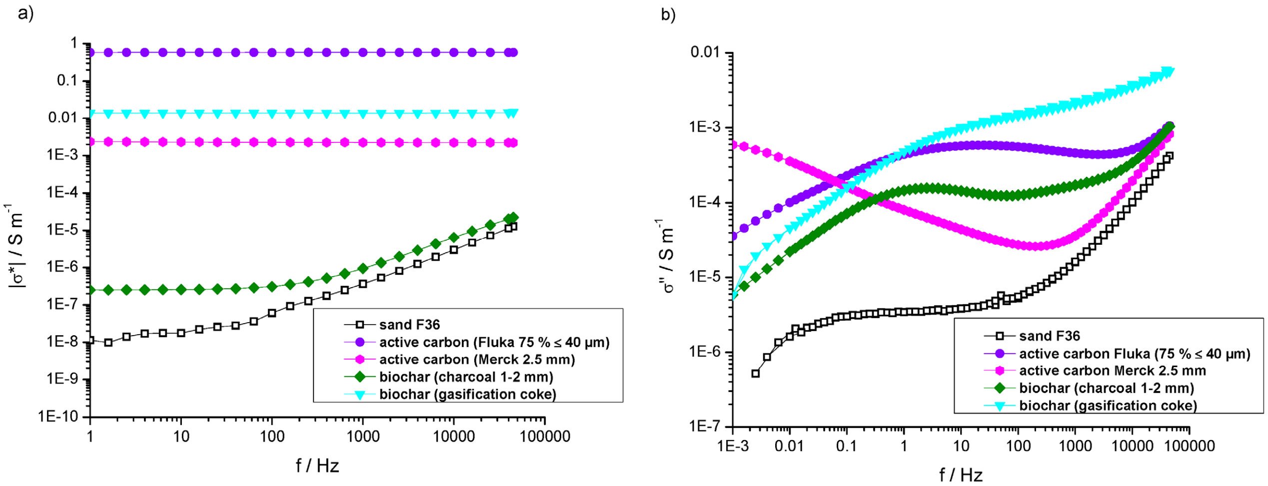

Fig. 2: a) Magnitude of the electrical conductivity of sand and different carbon materials. b) Imaginary part of the complex conductivity of sand with different carbon materials.

The frequency associated with maximum σ'' for active carbons and a series of different size fractions of the charcoal is dependent on the particle size, but two different lines are observed in a double logarithmic plot for charcoal and the active carbons with a slope that seems to be somewhat larger than expected for a diffusive relaxation mechanism (Fig. 3a). There is also some correlation between σ'' at a high frequency and the hydrogen/carbon ratio (Fig. 3b). This is related to the fact that the electronic conductivity increases, whereas leakage currents due to redox reactions and the hydrogen/carbon ratio decrease with increasing graphitization.

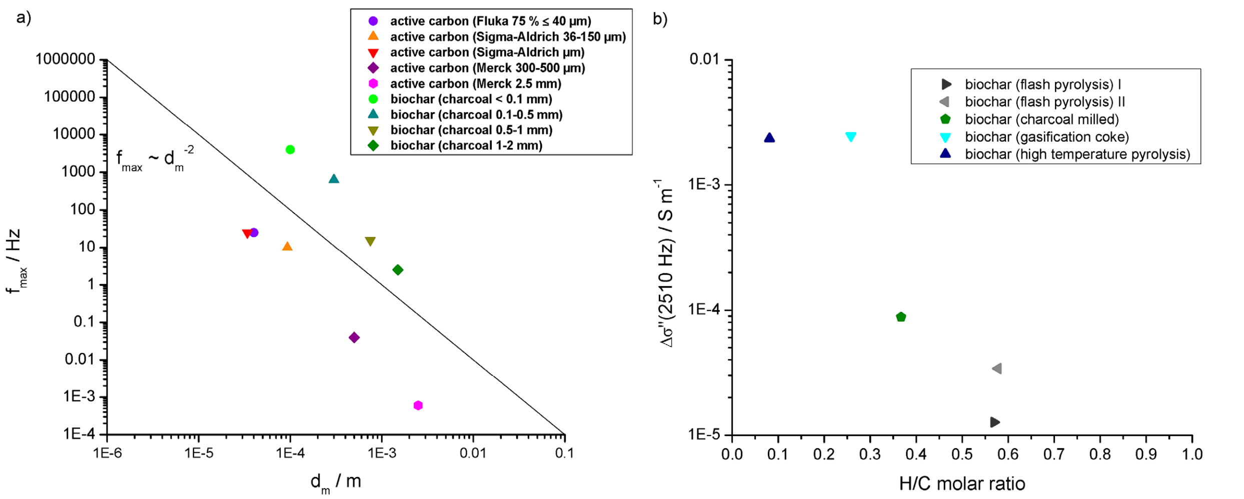

Fig. 3: a) Dependence of the maximum of σ'' on the particle size. b) Dependence of σ'' on the carbon/hydrogen ratio.

Conclusions

Electronic conductivity, particle size and H/C ratio influence the polarization of carbon material. Quantification of the effects still requires more data. We are currently extending our database with more measurements on a wide range of carbon materials.