

Review of Potential Models for Modeling CaCO_3 in the Development of Hydrogen Storage Material

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ABSTRACT

The use of hydrogen as a carrier fuel or clean energy is limited. At present, the hydrogen is produced by (i) steam methane reforming (SMR) (48%), (ii) gasifying coal (18%), (iii) reformed oil (30%) and, (iv) electrolysis (3.9%). Together, fossil fuel sources paths are needed if the hydrogen becomes a major source of energy for the future.

The main route for the production of hydrogen is by means of catalysis of methane with steam. This leads to a highly exothermic reaction generated from burners that produce and release CO_2 and high CO_2 emission caused by the increasing use of fossil fuels leads to an increase in the atmospheric concentration of CO_2 , causing global warming. CO_2 separation using conventional technologies such as adsorption, absorption, cryogenic distillation and membrane separation causes an increase in the production of electricity from 34-75%. While the efficient capture of CO_2 from these processes is favored at low temperatures and high pressures. An alternative to mitigate CO_2 emissions is through carbon capture and sequestration. Carbonation cycle and calcinations of an absorbent based on calcium oxide (CaO), calcium loop called, is a technology for CO_2 capture. A calcium loop system, CO_2 is a carbonator by the reaction between CaO and CO_2 in the adsorbent, wherein the adsorbent is then regenerated by calcination in the furnace by decomposition of CaCO_3 formed in the carbonation process.

In this work it make a review based on potential models for modeling CaCO_3 , considering a biodegradable material, the chicken eggshell as raw material for hydrogen storage.

1. Introduction

Inorganic chemical composition biomineral is dominated mainly by the calcium carbonate, which is found in biological systems in a number of different forms including the amorphous calcium carbonate (ACC), vaterite, aragonite and calcite. The first polymorphisms are less abundant in nature than the last two.

Polymorphs from calcium carbonate are minerals with the same chemical composition but a different arrangement of the ions in the crystal lattice. Calcium carbonate exists in six forms that are divided into three classes; anhydrous crystalline polymorphic forms (calcite, aragonite and vaterite) [1], hydrated crystalline forms (calcium carbonate monohydrate (MCC), calcium carbonate hexahydrate (ikaite)) and, amorphous calcium carbonate (ACC).

Aragonite is thermodynamically less stable than calcite. It has an orthorhombic crystal structure with the same alternating structure of Ca^{2+} and CO_3^{2-} ions as calcite. In aragonite, however, the CO_3^{2-} layers are split into layers parallel to the a axis and each Ca atoms surrounded by nine closest oxygen.

Vaterite is metastable with respect to calcite and aragonite and is rare in nature. It has a hexagonal crystal structure and a similar alternating structure with calcite and aragonite. In contrast to aragonite and calcite, the plane of CO_3 is parallel to the c axis.

Calcite is deposited extensively as a biomineral due to its high thermodynamically stability at ambient temperature. It has a rhombohedra crystal structure, consisting of Ca^{2+} ions and planar CO_3^{2-} groups, located in alternative layers and orientated perpendicular to the c axis. Each Ca^{2+} ion has six immediate CO_3^{2-} neighbors, oriented in such a way that one oxygen from each forms the immediate neighbors of calcium. This polymorphism of calcium carbonate is the one for the chicken eggshell [2].

2. Development

To describe the interatomic interactions of a system, a collection of parameters of mathematical functions has been used. In this publication presents a summary of interatomic potential functions. The atomic simulations are based on the Born model of solids, indicated that the interactions between the ions in the system are a combination of long-range electrostatic forces and short-range forces, both the repulsion and the van der Waals attractions between neighboring electron clouds. Known the potential energy of the system is the sum of the interactions between all ions.

$$U(r_{ij}) = \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \sum_{ij} \Phi_{ij}(r_{ij}) \quad (1)$$

$U(r_{ij})$, is the long-range electrostatic interactions between the ions, q_i and q_j are charges of the ions i and j respectively, r_{ij} is the distance between ions i and j , and ϵ_0 is the permittivity of free space. The right term represents the short-range forces, which are described and include primarily two-body interactions, for example, a

variation of the interaction of Ca-O in modeling of the CaCO_3 . Bond bending terms to convey the directionality of certain bonds in the crystal, for instance in the modeling of the covalent bonds in the carbonate group of CaCO_3 and four-body interactions such as dihedral terms.

The long-range electrostatic part of the potential energy of the equation of Born model is too slow to converge as a function of r_{ij} in real space. Has been used the Ewald summation method [3] to replaces the summation of potential energies in real space with an equivalent summation in Fourier space.

Each point charge in the system is viewed as being surrounded by a Gaussian charge distribution of equal and opposite sign, charge density is:

$$\rho_i(r_i) = \frac{q_i \alpha^3}{\pi^{3/2}} \exp(-\alpha^2 r_i^2) \quad (2)$$

Which α is a positive parameter that determines the width of the distribution, and r_i is the position relative to the centre of distribution. This introduced charge distribution screen the interaction between neighboring point-charges, effectively limiting them to a short range. Accordingly, the sum over all charges and their images in real space converges rapidly, which is:

$$U_{sr} = \frac{1}{2} \sum_{ij} q_i q_j \frac{\text{erfc}(\alpha r_{ij})}{r_{ij}} \quad (3)$$

$\text{erfc}(x)$ Is defined as the complimentary error function:

$$\text{erfc}(x) = 1 - \text{erf}(x) = 1 - \frac{2}{\pi^{1/2}} \int_0^x \exp(-u^2) du \quad (4)$$

A second Gaussian charge distribution of the same sign and magnitude as the original distribution is added in order to maintain the neutrality of charges. The sum is performed in the Fourier space to solve the resulting Poisson's equation.

$$U_{fr} = \frac{1}{2\pi V} \sum_{i,j} q_i q_j \sum_{m \neq 0} \frac{\exp[-(\pi m/\alpha)^2 + 2\pi m \cdot (r_i - r_j)]}{m^2} \quad (5)$$

Where m represent the reciprocal vectors and V is the volume of the unit cell of the crystal. Thereof, the correlation self-terms needs to be subtracted in order to cancel out the interaction of the introduced artificial counter-charges with itself. Then, the total electrostatic energy per unit cell can then be calculated:

$$\Phi_{ij} = U_{sr} + U_{fr} - \frac{\alpha}{\pi^{1/2}} \sum_i q_i^2 \quad (6)$$

Electronic polarisability is one way to include the electronic polarisability of the atoms is to use the core-shell model [4], where the polarisable ion is represented by a mass less shell connected to a core containing all the mass. The total charge of the ion is the sum of the charges of the core and shell. The position of the core represents the position of the ion in the crystal lattice and the position of the shell shows the electronic polarisability of the atom. The core and shell are connected by a harmonic spring. The spring constant K and the charge of the shell Ye determine the polarisability of the ion.

$$\alpha_p = \frac{Ye^2}{4\pi\epsilon_0 K} \quad (7)$$

Both K and Ye can be fitted empirically to reproduce experimental properties, such as dielectric and elastic constants. The short-range forces are assumed to act between the shells while the Coulombic forces act between all shells and cores, except between the core and shell of the same ion. The core-shell model has been successful in modeling various properties and it has been used in all static energy minimization calculations to describe the polarisability of the oxygen in the CO_3^{2-} group and water.

Short-range potential functions. The two-body potential functions act between neighboring charge clouds, the shells of the polarisable anions and the cores in the case of cations. They come in a number of analytical forms, all describing the potential energy as a function of inter-ionic separation. These potential functions act without taking into account directionality of any bonds. Three-body potential function acts between three ions and is used when covalent bonds are present in the system. The terms define angles and dihedrals between the ions and as such convey directionality to the bonds.

The Buckingham potential [5] is one of the most used functions for the interaction of two bodies which are not directly bonded.

$$\Phi_{ij}(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (8)$$

Where A_{ij} , ρ_{ij} and C_{ij} the parameters to describe the interaction between two atoms are i, j and r_{ij} is the inter-atomic distance. A_{ij} and ρ_{ij} are related to the number of electrons and the electron density respectively. The first term of the function describes the short-range repulsive interaction between the atoms, which originates from the Pauli Exclusion Principle, while the second represents the attractive van der Waals forces. Since, the exponential term converges to a constant as the distance r_{ij} approaches to zero, while the second term diverges, it runs the risk of

an un-physical “Buckingham catastrophe”, when used in simulation of charged systems. This occurs when the electrostatic attraction artificially overcome the repulsive barrier [6]. Minimizing the energy of a structure which accidentally has a very short distance between two atoms will thus result in “nuclear fusion”.

Morse potential function [7] is used for modeling covalent bonds and capable of modeling harmonicity. As such interatomic distances away from the equilibrium bond distance can be simulated reliably with this potential function, the carbon-oxygen bond in the CO_3^{2-} .

$$\Phi_{ij}(r_{ij}) = D_{ij} \left(1 - e^{-\alpha(r_{ij}-r_0)} \right)^2 \quad (9)$$

Where D_{ij} is the depth of the potential well, i.e. the thermodynamic dissociation energy of the bond, r_0 is the equilibrium bond length, and α is a constant controlling the “width” of the potential. The form of the Morse potential function ensures that at infinite separation of the two atoms the potential energy is zero while the potential energy is at a minimum at the equilibrium bond distance. Sometimes the Morse potential is used with subtraction of the Coulombic interaction and as such it is the only potential function describing a bond between two nearest neighbors. Interactions between second and further nearest neighbors can be described by Coulombic interactions and another short-range potential function.

The Lennard-Jones potential [8], the commonest form is also referred to as the 6-12 potential, is one of the most used potential functions to approximate the interaction between a pair of atoms.

$$\Phi_{ij}(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6} \quad (10)$$

Taking $A = 4\epsilon\sigma^{12}$ and $B = 4\epsilon\sigma^6$, with ϵ is the depth of the potential well and σ is the finite distance where the interparticle potential is zero. The repulsive part is dependent on r^{-12} and thus acts at close range, while the attractive part is proportional to r^{-6} and becomes dominant at longer range. The parameters can be fitted to reproduce experimental data or accurate quantum chemistry calculations. Due to its computational simplicity, the Lennard-Jones potential is used extensively in computer simulations even though more accurate potentials exist.

Many body potential function. The three-body harmonic potential is used to describe the partial co-valence in the CO_3^{2-} group and maintain the bond angle between two carbon-oxygen bonds.

$$\Phi_{ijk}(\theta_{ijk}) = \frac{1}{2} k_{ijk} (\theta_{ijk} - \theta_0)^2 \quad (11)$$

Tacking k_{ijk} is the force constant and $(\theta_{ijk} - \theta_0)$ is the deviation from the equilibrium angle θ_0 . The function acts between a central ion i and two ions j and k bonded to i making the bond angle θ_{ijk} .

The four-body out of plane potential is applied to planar arrangements of three bonds or torsional angles. The four-body potential function for the CO_3^{2-} group is described as said Pavese et al. [9].

$$\Phi_{ijkl} = k_{ijkl}[1 - s \cos(N\theta)] \quad (12)$$

Tacking k_{ijkl} is the force constant s is ± 1 and N is an integer which gives the periodicity of the torsion, which to be 2 in the case of the planar CO_3^{2-} group. The above functional form means that the energy has a minimum vale when θ is 0 or π radians and all atoms lie the same plane in the CO_3^{2-} group.

3. Conclusions

The potential parameters of calcite that will be used have been derived empirically from Pavese et al., in a study of the thermal dependence of structural and elastic properties of calcite. The oxygen-oxygen and, calcium-oxygen interactions will be modeled by Buckingham potential. The co-valence within the CO_3^{2-} group modeled by a Morse potential plus a three-body potential and torsional potential function to restrain the planar CO_3^{2-} group from folding.

4. References

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