



Density functional theory study of oxygen migration in molten carbonate



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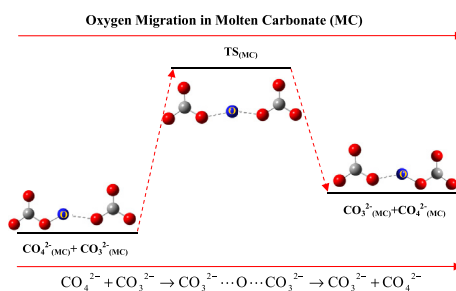
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HIGHLIGHTS

- The process of oxygen migration in MC has been examined using DFT.
- A cooperative “cogwheel” mechanism is proposed.
- The lower energy barriers indicate that oxygen transfer in MC is fairly easy.
- The results imply that ORR in MC modified cathodes is facilitated.

GRAPHICAL ABSTRACT



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ABSTRACT

The process of oxygen migration in alkali molten carbonate salts has been examined using density functional theory method. All geometries were optimized at the B3LYP/6-31G(d) level, while single point energy corrections were performed using MP4 and CCSD(T). At TS, a O–O–O linkage is formed and O–O bond forming and breaking is concerted. A cooperative “cogwheel” mechanism as described in the equation of $\text{CO}_4^{2-} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{2-} \cdots \text{O} \cdots \text{CO}_3^{2-} \rightarrow \text{CO}_3^{2-} + \text{CO}_4^{2-}$ is involved. The energy barrier is calculated to be 103.0, 136.3 and 127.9 kJ/mol through an intra-carbonate pathway in lithium, sodium and potassium carbonate, respectively. The reliability and accuracy of B3LYP/6-31G(d) were confirmed by CCSD(T). The calculated low values of activation energy indicate that the oxygen transfer in molten carbonate salts is fairly easy. In addition, it is found that lithium carbonate is not only a favorable molten carbonate salt for better cathode kinetics, but also it is widely used for reducing the melting point of Li/Na and Li/K eutectic MC mixtures. The current results imply that the process of oxygen reduction in MC modified cathodes is facilitated by the presence of MC, resulting in an enhancement of cell performance at low operating temperatures.

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1. Introduction

Solid oxide fuel cells (SOFCs) have received considerable

attention for the purpose of clean energy with high efficiency and fuel flexibility [1–3]. However, conventional SOFCs only operate at high temperatures of the range 800–1000 °C, which leads to both technical challenges and high cost in fabrication. Both are main impendence for the commercialization of SOFCs. One of the key solutions to address this issue is to lower the operating temperature under 600 °C, where higher reliability and lower cost can be

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achieved. Recently, it has been reported that binary or ternary molten carbonate (MC) compositions incorporated into the solid electrolyte or cathode can lower the operating temperature, strengthen mechanical properties, yield high power density, and result in excellent cell performances [4–15]. For example, a samarium doped ceria (SDC) electrolyte with $(\text{Li}_{0.52}/\text{Na}_{0.48})_2\text{CO}_3$ (30 wt.% loading) was used in SOFCs and the cell reached the maximum power density (P_{max}) of 1704 mW cm^{-2} at $650 \text{ }^\circ\text{C}$ [5]. Zhu et al. examined a series of ceria-based two-phase composite electrolyte materials and found ceria/MC composites very competitive for SOFCs operated at $<600 \text{ }^\circ\text{C}$ [6–8]. Previous work by Huang et al. [9–11] also indicates that the presence of MC phase in the cathode of SOFC significantly reduces the cathode area specific resistance (ASR) and polarization resistance (R_p) by a factor of 10. This implies that the oxygen reduction reaction (ORR) has been remarkably enhanced and the operating temperature of SOFCs can then be largely reduced. Similarly, Bodén et al. [12] found that the proton conductivity of SDC-Li/Na carbonate composite increases as the content of carbonate salt increases. On the other hand, Xie et al. [13] predicted that a composite electrolyte of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mn}_{0.2}\text{O}_{2.85}$ with eutectic carbonate ($\text{Li}_2\text{CO}_3:\text{Na}_2\text{CO}_3 = 52:48$) is a promising candidate for long-term low temperature SOFCs due to its notable thermal stability and fairly high performance.

All the evidences indicate that the presence of a MC phase not only enhances the ionic conductivity, but also improves the kinetics of the ORR process. It is well understood that the ORR process is a crucial step for the cathode of SOFCs. It only occurs at the so-called triple phase boundary (TPB) region as displayed in Fig. 1. TPB is a very small overlap between feeding gas, electrolyte and cathode, acting like a bridge for oxygen ion migration from cathode to electrolyte. Unfortunately, the rate of migration is largely limited by the available surface at TPB. With the presence of MC at TPB, the new micro-MC phase will provide much more surface area than the TPB itself for the oxygen ion migration. On the other hand, it will facilitate the adsorption and dissociation of oxygen on the MC treated cathode surface, resulting in better cathode kinetics.

To understand the mechanism of ORR with the presence of MC in fuel cells, both theoretical and experimental efforts have been carried out. Huang et al. proposed a new ORR charge-transfer model involving MC phase [15] and the ORR pathways in the presence of MCs [11]. In our recent work [16], the change of energy is calculated to be -101.7 kJ/mol for the reaction of $\text{CO}_3^{2-} + \text{O}_2 \rightarrow \text{CO}_5^{2-}$, indicating that the adsorption of O_2 on the MC surface is thermodynamically favorable. The equilibrium constant of 1.1 at 873 K for the subsequent reaction of $\text{CO}_5^{2-} + \text{CO}_3^{2-} \leftrightarrow 2\text{CO}_4^{2-}$ indicates that the CO_4^{2-} is a vital intermediate and oxygen carrier. The existence of CO_4^{2-} is then verified by in-situ Raman spectroscopy [17]. In Refs. [18], the oxygen dissociation reaction in alkali

molten carbonate has been systematically studied. The energy barrier is calculated to be 197.9, 116.7, and 170.3 kJ/mol in the $(\text{M}_2\text{CO}_3)_4$ cluster, $\text{M} = \text{Li}, \text{Na}, \text{and K}$, respectively. It is very clear that the molten carbonate salt has directly participated in the ORR process and plays an important role as a catalyst in the cathode of SOFCs.

For oxygen migration from the MC surface to MC/cathode interface, Huang et al. [15] proposed a cooperative “cogwheel” mechanism, involving the breaking and reforming of the $\text{O} - \text{CO}_3^{2-}$ bond. However, this assumption has not been verified yet by experiments or theoretical simulations. Up to date, only very little information about oxygen transfer in MC has been reported in the literature. In the current study, we focus mainly on the process of oxygen migration in alkali molten carbonate salts, especially its energetics and pathways. The aim is to provide theoretical foundations for understanding oxygen migration in different molten carbonate salts. The transition states, activation energies and reaction pathways are investigated using density functional theory (DFT) calculations.

2. Computational methods

All calculations were performed in Gaussian09 suite of quantum programs [19]. Local minimum structures were optimized at the B3LYP [20,21]/6-31G(d) [22–25] level. Vibrational frequencies were examined to ensure that the reactant and product structures are local minima while each transition state (TS) is a first-order saddle point on the potential energy surface (PES). Both MP4 [26] and CCSD(T) [27,28] in combination with variable basis sets (6-311G++(d) [29–31], CBSB7 [32], and LANL2DZ [33,34]) were used to assure the accuracy and reliability of the energy values obtained at the B3LYP/6-31G(d) level. In addition, the zero-point energy (ZPE) and Mulliken charges were calculated and discussed.

In order to elucidate the process of oxygen migration in MC, a four-formula cluster $(\text{M}_2\text{CO}_3)_4$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$), was used as the surrogate of the molten state of alkali carbonate, which is shown in Fig. 2. The structures were optimized at the B3LYP/6-31G(d) level and showed very good agreement with the previous report in Ref. [18]. The structure of each transition state was initially identified using PES scan method, i.e. the highest energy point on PES. The geometry was then optimized with full relaxation and confirmed to be a saddle point on PES. The intrinsic reaction coordinate (IRC) calculations were used to determine the reaction path.

3. Results and discussions

3.1. Intramolecular migration of oxygen in carbonate ion

Fig. 3 shows the structures of beginning, transitioning and ending phase of the intramolecular transfer of oxygen in CO_3^{2-} together with bond distances and relative energies. The reactant and product are identical CO_4^{2-} with a C_s symmetry, while O5 is bonded to O4 and O2, respectively. Therefore, only the reactant structure is discussed here. Once O5 is attached to the carbonate and the O5–O4 bond is formed, C1–O4 is weakened with a bond distance of 1.387 \AA (Note: the C–O distance in CO_3^{2-} is optimized to be 1.313 \AA). Both C1–O2 and C1–O3 are shortened to 1.263 \AA and 1.285 \AA , respectively. The resonance structure of carbonate unit has been largely weakened. The Mulliken charge on O4–O5 is calculated to be $-1.13 e$ and its bond distance is 1.496 \AA , both indicating O4–O5 a fragment between superoxide and peroxide. The stretching of O4–O5 leads to a TS on PES. At TS, O5–O4 is 2.304 \AA as same as O5–O2, showing that O5–O4 is breaking and O5–O2 is forming along the reaction coordinator. Furthermore, O5 is almost

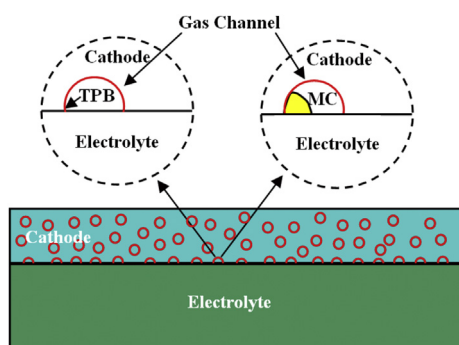


Fig. 1. Illustration of oxygen reduction reaction in SOFCs (Left: No MC, Right: With MC).

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