

6-11-2013

## First Spectroscopic Identification of Pyrocarbonate for High CO<sub>2</sub> Flux Membranes Containing Highly Interconnected Three Dimensional Ionic Channels

Lingling Zhang

University of South Carolina - Columbia, zhang257@cec.sc.edu

Xinyu Huang

University of South Carolina - Columbia, xyhuang@sc.edu

Changyong Qin

Kyle Brinkman

Yunhui Gong

Follow this and additional works at: [https://scholarcommons.sc.edu/emec\\_facpub](https://scholarcommons.sc.edu/emec_facpub)

 [Click the next page for additional authors](#)  
Part of the [Mechanical Engineering Commons](#)

---

### Publication Info

Published in *Physical Chemistry Chemical Physics*, Volume 15, Issue 31, 2013, pages 13147-13152.

©Physical Chemistry Chemical Physics (2013), Royal Society of Chemistry.

This article cannot be redistributed or further made available.

This article was first published by the Royal Society of Chemistry and can be found at <http://dx.doi.org/10.1039/C3CP52362D>

Zhang, L., Huang, X., Qin, C., Brinkman, K., Gong, Y., Wang, S., & Huang, K. (2013). First Spectroscopic Identification of Pyrocarbonate for High CO<sub>2</sub> Flux Membranes Containing Highly Interconnected Three Dimensional Ionic Channels. *Physical Chemistry Chemical Physics*, 15 (31), 13147 - 13152.  
<http://dx.doi.org/10.1039/C3CP52362D>

This Article is brought to you by the Mechanical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact [digres@mailbox.sc.edu](mailto:digres@mailbox.sc.edu).

---

**Author(s)**

Lingling Zhang, Xinyu Huang, Changyong Qin, Kyle Brinkman, Yunhui Gong, Siwei Wang, and Kevin Huang

# First spectroscopic identification of pyrocarbonate for high CO<sub>2</sub> flux membranes containing highly interconnected three dimensional ionic channels

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 13147

Lingling Zhang,<sup>a</sup> Xinyu Huang,<sup>a</sup> Changyong Qin,<sup>b</sup> Kyle Brinkman,<sup>c</sup> Yunhui Gong,<sup>a</sup> Siwei Wang<sup>a</sup> and Kevin Huang<sup>\*a</sup>

Identification of the existence of pyrocarbonate ion C<sub>2</sub>O<sub>5</sub><sup>2-</sup> in molten carbonates exposed to a CO<sub>2</sub> atmosphere provides key support for a newly established bi-ionic transport model that explains the mechanisms of high CO<sub>2</sub> permeation flux observed in mixed oxide-ion and carbonate-ion conducting (MOCC) membranes containing highly interconnected three dimensional ionic channels. Here we report the first Raman spectroscopic evidence of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> as an active species involved in the CO<sub>2</sub>-transport process of MOCC membranes exposed to a CO<sub>2</sub> atmosphere. The two new broad peaks centered at 1317 cm<sup>-1</sup> and 1582 cm<sup>-1</sup> are identified as the characteristic frequencies of the C<sub>2</sub>O<sub>5</sub><sup>2-</sup> species. The measured characteristic Raman frequencies of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> are in excellent agreement with the DFT-model consisting of six overlapping individual theoretical bands calculated from Li<sub>2</sub>C<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>5</sub>.

Received 6th June 2013,

Accepted 6th June 2013

DOI: 10.1039/c3cp52362d

[www.rsc.org/pccp](http://www.rsc.org/pccp)

## Introduction

Manmade CO<sub>2</sub> emission through the use of fossil fuels is thought to be a major source for global warming and climate change. The stabilization of atmospheric CO<sub>2</sub> concentration is generally considered as the best near-term solution to mitigate the negative environmental impacts caused by burning fossil fuels. The current mainstream technical approach to achieving that goal is to curb the emission of CO<sub>2</sub> by capturing CO<sub>2</sub> at point-sources and geologically storing it. So far, three industrial combustion processes have been identified as the point-sources for carbon removal:<sup>1–10</sup> pre-combustion, post-combustion and oxy-combustion. Significant technical progress in materials development and engineering design of carbon capture systems has been made over the past few decades, but the major challenge to the commercial deployment of these technologies remains to be the energy penalty associated with CO<sub>2</sub> capture, compression and storage (CCS) that considerably lowers the overall plant efficiency and ultimately increases the cost-of-electricity produced.

The state-of-the-art technologies for CO<sub>2</sub>-capture are principally based on reversible chemical–physical sorption processes using

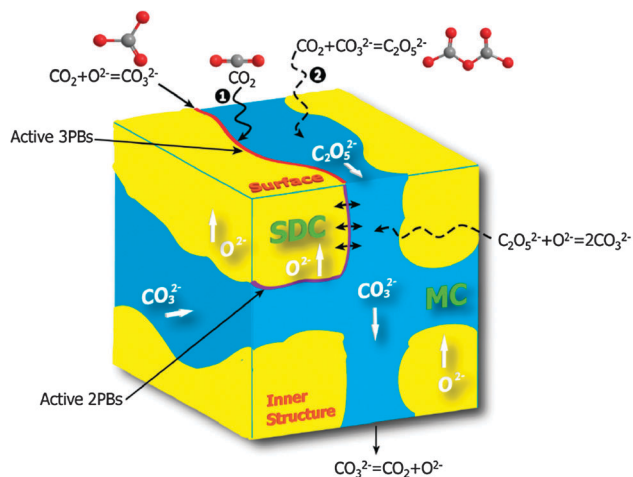
liquid solvents and solid sorbents as CO<sub>2</sub> scrubbers<sup>11–13</sup> and on size-exclusion permeation using membranes as CO<sub>2</sub> molecular filters.<sup>14–19</sup> However, as aforementioned, the solvents and sorbents based technology is cost prohibitive and energy intensive,<sup>20–24</sup> and the membrane technology is susceptible to poor selectivity and incompatibility at high temperatures.<sup>25–28</sup> As of today, only a few of these technologies are considered commercially ready for large-scale application.

In an effort to advance the CCS technology, we as well as other research groups have recently studied a new type of electrochemical CO<sub>2</sub> separation membranes that are in theory exclusively permeable to CO<sub>2</sub> and compatible with elevated temperatures.<sup>5,29–33</sup> The new electrochemical membranes consist of an oxide-ion conducting porous matrix densely filled with a carbonate-ion conducting alkali carbonate melt, which constitutes a dual-phase mixed oxide-ion and carbonate-ion conductor (MOCC). CO<sub>2</sub> is transported through the membrane in the form of CO<sub>3</sub><sup>2-</sup>, which is charge-compensated by a concomitant flow of O<sup>2-</sup>. Therefore, the MOCC membranes are more suited for pre-combustion application where the feedstock gas is a mixture of CO<sub>2</sub> and H<sub>2</sub>. We have particularly shown that the solid oxide-ion conductor of the porous matrix synthesized using a combined “co-precipitation” and “sacrificial-template” method encompasses abundant highly-interconnected ionic channels with well-defined and tunable microstructural features for fast CO<sub>2</sub> transport.<sup>5,34,35</sup> The CO<sub>2</sub> permeation flux density measured from these membranes exposed to CO<sub>2</sub>–H<sub>2</sub>

<sup>a</sup> Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29201, USA. E-mail: [kevin.huang@sc.edu](mailto:kevin.huang@sc.edu)

<sup>b</sup> Department of Biology, Chemistry and Environmental Health Science, Benedict College, Columbia, South Carolina 29204, USA

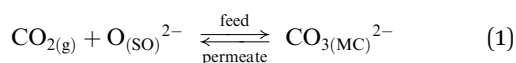
<sup>c</sup> Materials Science & Technology, Savannah River National Laboratory, Aiken, SC 29808, USA



**Fig. 1** A 3D-schematic illustrating electrochemical reaction occurring at 3PBs to 2PBs in dual-phase MOCC membranes; SDC = Sm<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub>; MC = molten carbonate.

feed gas is remarkable, attaining  $J_{\text{CO}_2} \geq 1 \text{ mL min}^{-1} \text{ cm}^{-2}$  and averaging nearly two orders of magnitude higher than membranes developed by other groups.<sup>30,31</sup>

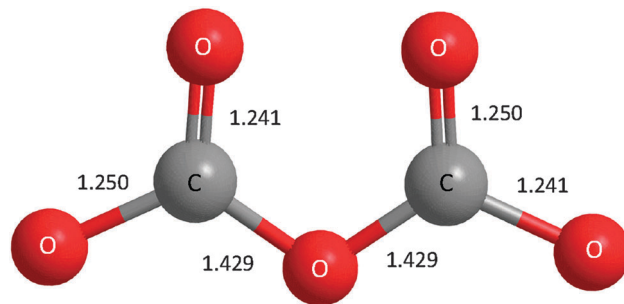
To understand the fundamentals of a high-flux CO<sub>2</sub> transport phenomenon through the MOCC membranes, we propose for the first time a multi-pathway bi-ionic transport model schematically shown in Fig. 1. The core of the new model is an ionic pathway (denoted as Pathway-2) along the two-phase boundaries (2PBs) between solid-oxide and molten-carbonate (MC), which is parallel to the ionic pathway at the three-phase-boundaries (3PBs) (denoted as Pathway-1). The Pathway-1 is a conventional route that considers surface ionization of CO<sub>2</sub> solely at 3PBs, where CO<sub>2</sub>, O<sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> are simultaneously available at the feed surface, and subsequent transport of CO<sub>3</sub><sup>2-</sup> through the MC phase and deionization of CO<sub>3</sub><sup>2-</sup> on the permeate surface.



Here the subscripts (g), (SO) and (MC) represent gas, solid-oxide and molten carbonate phases, respectively. During the CO<sub>2</sub> transport, the flux of CO<sub>3</sub><sup>2-</sup> is charge-compensated by the flow of O<sup>2-</sup>. The theoretical CO<sub>2</sub> flux density  $J_{\text{CO}_2}$  through 3PBs can be calculated by<sup>5</sup>

$$J_{\text{CO}_2} = -\left(\frac{\varepsilon}{\tau}\right) \frac{RT}{4F^2 L} \frac{\varphi \sigma_c (1 - \varphi) \sigma_o}{\varphi \sigma_c + (1 - \varphi) \sigma_o} \ln \frac{P'_{\text{CO}_2}}{P''_{\text{CO}_2}} \quad (2)$$

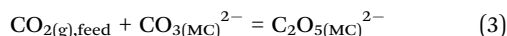
Here  $\varepsilon$  and  $\tau$  are the porosity and tortuosity of the porous oxide matrix, respectively;  $\sigma_c$  and  $\sigma_o$  are ionic conductivities of the carbonate ion and the oxide ion, respectively;  $P'_{\text{CO}_2}$  and  $P''_{\text{CO}_2}$  are the partial pressure of CO<sub>2</sub> at the feed and permeate sides, respectively;  $\varphi$  is the volumetric fraction of the MC phase;  $L$  is the thickness of the membrane, and  $R$ ,  $T$  and  $F$  have their usual meanings. The CO<sub>2</sub> ionization reaction (1) has been widely suggested in the literature as the global mechanism for CO<sub>2</sub>



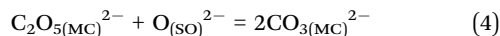
**Fig. 2** Equilibrium geometry of the C<sub>2</sub>O<sub>5</sub><sup>2-</sup> species. The unit of bond length is in Å.

transport in dual-phase MOCC, but proceeding at a relatively slow rate.<sup>36–38</sup>

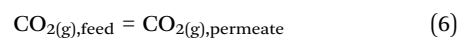
The Pathway-2 encompasses surface ionization of CO<sub>2</sub> at 2PBs of the CO<sub>2</sub>/MC interface and internal ionic transfer at 2PBs of the SDC/MC interface. The species C<sub>2</sub>O<sub>5</sub><sup>2-</sup> (pyrocarbonate or dicarbonate anion) possessing a (CO<sub>2</sub>)<sub>n</sub> chainlike structure as shown in Fig. 2 is deemed an intermediate product of CO<sub>2</sub> chemisorption on the surface of MC *via*



Once formed, C<sub>2</sub>O<sub>5</sub><sup>2-</sup> can immediately react with O<sup>2-</sup> available at the SDC/MC interface, dissociating into two CO<sub>3</sub><sup>2-</sup> that can migrate to 3PBs on the permeate surface, where much faster CO<sub>3</sub><sup>2-</sup> deionization reaction takes place to release CO<sub>2</sub> and O<sup>2-</sup>.



The overall reaction of the CO<sub>2</sub>-transport is, therefore, given by



Overall, the reactive zones for the CO<sub>2</sub>-transport are extended from 3PBs to 2PBs, significantly increasing the reactive areas, thus being largely responsible for the observed high CO<sub>2</sub> flux. Key support to the above new bi-ionic transport model is the experimental evidence of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> existing on the surface of a MC exposed to a CO<sub>2</sub> atmosphere. The likelihood of absorbing CO<sub>2</sub> on the surface of a MC to form C<sub>2</sub>O<sub>5</sub><sup>2-</sup> has been suggested by Claes *et al.*<sup>36–38</sup> who studied the solubility and solvation of CO<sub>2</sub> in a molten eutectic mixture of Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> at 973 K. They found CO<sub>2</sub> to be extremely soluble in MC. The measured 0.1 mol per liter per atm solubility is well beyond what is expected from Henry's law. The authors concluded that chemical absorption was taking place, most probably by the reaction of CO<sub>3(MC)</sub><sup>2-</sup> + CO<sub>2(g)</sub> = C<sub>2</sub>O<sub>5(MC)</sub><sup>2-</sup>. DFT calculations were carried out by the authors to gain insight into the reaction energetics. The calculated values for  $\Delta H^0$  and  $\Delta G^0$  are –223 kJ mol<sup>–1</sup> and –119 kJ mol<sup>–1</sup> at 973K, respectively, indicating favorable gas-phase energetics, and solvation should not hinder the formation of the postulated C<sub>2</sub>O<sub>5</sub><sup>2-</sup> in the MC. Furthermore, another study reported cross-over <sup>13</sup>C-NMR experiments between [<sup>13</sup>C] and [<sup>18</sup>O] carbonates

in aqueous solutions of  $\text{Na}_2\text{CO}_3$ .<sup>39</sup> The complex kinetic problem was interpreted as giving evidence for the existence of the  $\text{CO}_3^{2-}(\text{aq}) + \text{CO}_2(\text{g}) = \text{C}_2\text{O}_5^{2-}(\text{aq})$  equilibrium under these experimental conditions. Based on these early studies, it is, therefore, conceivable that the formation of  $\text{C}_2\text{O}_5^{2-}$  species in MC by chemical absorption of  $\text{CO}_2$  could well be a facile process. However, so far no direct experimental observation of the existence of  $\text{C}_2\text{O}_5^{2-}$  species in MC has been reported.

Here we report for the first time spectroscopic observation of the  $\text{C}_2\text{O}_5^{2-}$  species in a  $\text{Li}_2\text{CO}_3$ – $\text{Na}_2\text{CO}_3$  melt surrounded by a  $\text{CO}_2$  atmosphere. A standard procedure to identify newly synthesized compounds or species in the chemical world is to record IR and Raman vibrational spectra. This procedure is relevant as long as the vibrational spectrum is not too congested (which usually happens below  $900\text{ cm}^{-1}$  because of the superposition of bending, rocking, and torsional modes). *In situ* Raman spectroscopy is, therefore, chosen as the method of study to probe  $\text{C}_2\text{O}_5^{2-}$  species.

## Experimental procedures

### *In situ* Raman spectroscopic study

The  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  eutectic mixture (52 : 48 in mol%) was first synthesized in air at  $650\text{ }^\circ\text{C}$ . After a 2 h hold, the melt was then quenched to room temperature, followed by breaking into fine particles by ball milling. Thus prepared powders were then packed into a gold crucible that was subsequently loaded into a high temperature stage (Linkam TS1500, 0– $1500\text{ }^\circ\text{C}$ ). The temperature and gas were controlled using a system controller (Linkam PE95). The Raman spectra were recorded using a LabRam/HR confocal Raman system (LabRam Invers, Horiba Jobin-Yvon) with a He–Ne laser operated at  $632.8\text{ nm}$ . Since the position of the thermocouple in the high temperature stage is located outside the crucible, the actual and the controlled temperatures of the MC are different. The melting point of the  $(\text{Li}/\text{Na})_2\text{CO}_3$  at  $490\text{ }^\circ\text{C}$  was used to calibrate the actual temperature. The scattering Raman spectra were collected *in situ* from the carbonate as a function of temperature (in the range of RT– $600\text{ }^\circ\text{C}$ ) and atmosphere (in  $\text{N}_2$ , air,  $\text{CO}_2$ ).

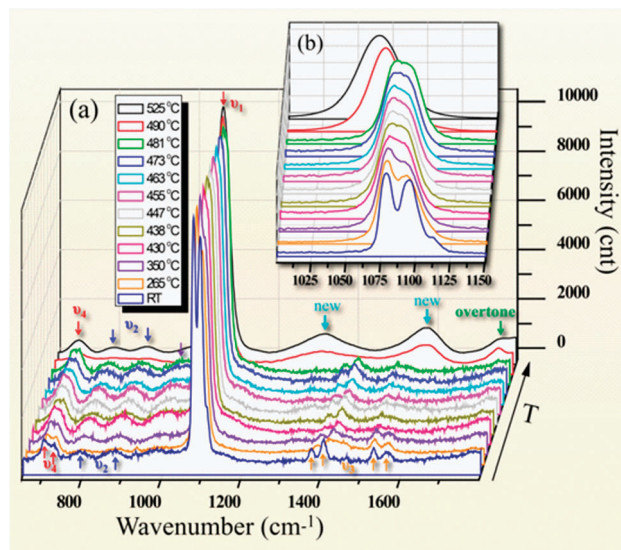
### DFT modeling

DFT calculations were performed at the B3LYP/6-31G(d)<sup>40–44</sup> level using the Gaussian09<sup>45</sup> suite of quantum programs. The geometry of  $\text{Li}_2\text{C}_2\text{O}_5$  and  $\text{Na}_2\text{C}_2\text{O}_5$  was optimized first, and the vibrational frequencies were then obtained from analytic second derivatives using a harmonic oscillator model. In addition, Raman intensities were computed by numerical differentiation of dipole derivatives with respect to the electric field.<sup>46</sup>

## Results and discussion

### Temperature dependence of the Raman spectrum

Fig. 3(a) shows the Raman spectra collected from a eutectic  $\text{Li}_2\text{CO}_3$ – $\text{Na}_2\text{CO}_3$  (52 mol%  $\text{Li}_2\text{CO}_3$ – $\text{Na}_2\text{CO}_3$ ) melt over a band range of  $650$ – $1850\text{ cm}^{-1}$  as a function of temperature in a pure  $\text{CO}_2$  atmosphere. For the carbonate in the solid state, the



**Fig. 3** (a) The Raman spectra of  $(\text{Li}/\text{Na})_2\text{CO}_3$  in the region of  $650$ – $1850\text{ cm}^{-1}$  as a function of temperature in a  $\text{CO}_2$  atmosphere; (b) magnified view in the region of  $1000$ – $1150\text{ cm}^{-1}$ .

Raman spectra are seen to contain four basic vibrational modes relevant to  $\text{CO}_3^{2-}$  ions. The two bands at  $1078$  and  $1094\text{ cm}^{-1}$  are assigned to  $\nu_1$  of symmetric stretching vibrations in  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ , whereas the bands at  $792\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  are assigned to  $\nu_2$  of out-of-plane bending vibrations.<sup>47–49</sup> For the isolated  $\text{CO}_3^{2-}$  that has a  $D_{3h}$  symmetry,  $\nu_2$  is Raman inactive. However, it is likely that  $\nu_2$  becomes Raman active for  $(\text{Li}/\text{Na})_2\text{CO}_3$  due to the distortion of the  $\text{CO}_3^{2-}$  structure imposed by the cations.<sup>50</sup> The observed bands at  $704$  and  $728\text{ cm}^{-1}$  are assigned to  $\nu_4$  of in-plane bending vibrations. This mode is a double degeneration for the distorted  $\text{CO}_3^{2-}$  induced by  $\text{Li}^+$  and  $\text{Na}^+$ . As the  $\text{CO}_3^{2-}$  group becomes distorted from its regular planar symmetry, this mode splits into two components.<sup>51</sup> The bands at  $1375\text{ cm}^{-1}$ ,  $1404\text{ cm}^{-1}$ ,  $1531\text{ cm}^{-1}$  and  $1563\text{ cm}^{-1}$  are attributed to a split  $\nu_3$  of the asymmetric stretching vibrations caused by the existence of  $\text{Li}^+$  and  $\text{Na}^+$  around the  $\text{CO}_3^{2-}$  ions.<sup>50</sup>

The shift of the Raman band with temperature is better viewed in Fig. 3(b), a magnified spectrum showing the region of the major  $\nu_1$ -bands at  $1078\text{ cm}^{-1}$  and  $1094\text{ cm}^{-1}$ . As the temperature increases, the  $\nu_1$ -bands for  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  shift toward a lower wavenumber and eventually merge into one broad peak at the melting temperature of  $490\text{ }^\circ\text{C}$ . This shift is a direct result of lowered force-constant, elongated C–O bond length and weakened Li(Na)–C–O bond strength by increasing temperature.<sup>52</sup> When the temperature reaches the melting point, the overtone of the out-of-plane bending mode ( $2\nu_2$ ) appears at  $1762\text{ cm}^{-1}$ .<sup>53</sup> It should be noted that a broad but small peak near  $970\text{ cm}^{-1}$  only observed in solid-state carbonates appears not to be directly related to  $\text{CO}_3^{2-}$ , identification of which is not possible for this study. We speculate that the impurities in the sample could be a source for this unknown peak. A detailed assignment of the measured Raman bands at different temperatures and atmospheres is summarized in Table 1.



**Table 1** The Raman frequencies measured and assigned for the eutectic (Li/Na)<sub>2</sub>CO<sub>3</sub> at selected temperatures and atmospheres

Atmospheres	CO <sub>2</sub>				Air	N <sub>2</sub>
Temperatures (°C)	RT	350	455	490 (melted)	490 (melted)	490 (melted)
Frequencies (cm <sup>-1</sup> )	704	706	706	707	707	707
$\nu_4$ (weak)	728	720	715	—	—	—
	792	790	789	790	790	790
$\nu_2$ (weak)	879	879	881	882	885	885
	1078	1077	1077	1070	1072	1072
$\nu_1$ (strong)	1094	1090	1087	—	—	—
	1375	1385	1386	—	1391	1392
	1404	1415	1416	—	1421	1421
$\nu_3$ (weak)	1531	1520	1520	—	—	—
	1563	1555	1545	—	—	—
New peaks (broad)	—	—	—	1317	—	—
	—	—	—	1582	—	—
Overtone ( $2\nu_2$ )	—	—	—	1762	1762	1762
Unknown	—	—	972	—	—	—

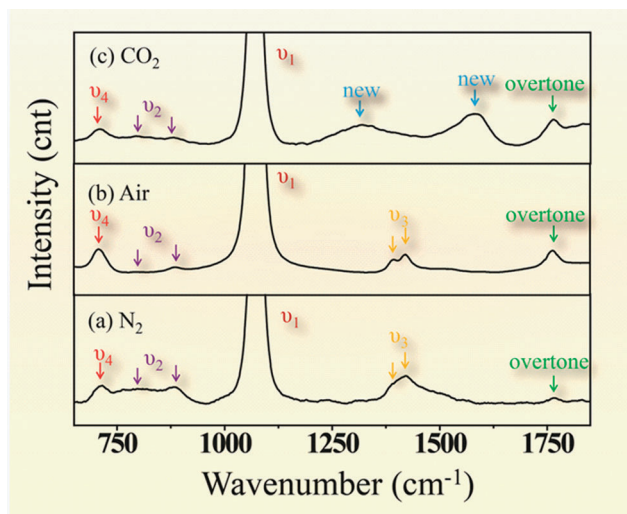
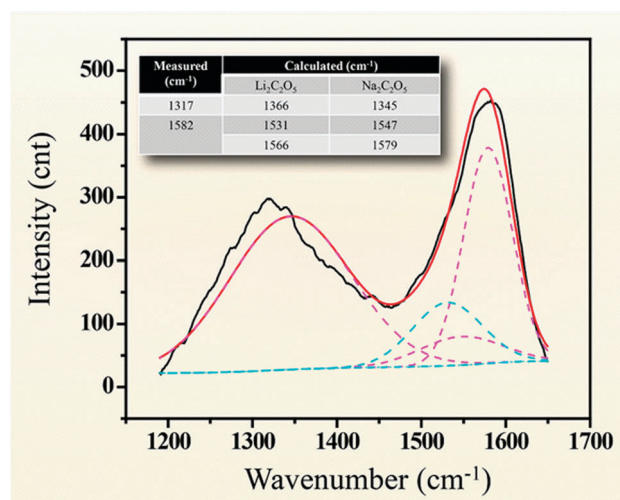
The most distinguishable features of Raman spectra in Fig. 3 are observed when the carbonate is in a molten state. The four bands corresponding to the  $\nu_3$  mode disappear from the spectrum while two new broad bands at 1317 cm<sup>-1</sup> and 1582 cm<sup>-1</sup> emerge within the same band width. A natural question to ask is: are these newly emerged Raman bands associated with the C<sub>2</sub>O<sub>5</sub><sup>2-</sup> species?

#### Atmosphere-dependence of the Raman spectrum

To answer this question, we first measured Raman spectra in different atmospheres. According to the enabling electrochemical reaction shown in reaction (3), the formation of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> requires a source of CO<sub>2</sub>. Fig. 4 compares the Raman spectra measured in N<sub>2</sub>, air and pure CO<sub>2</sub> atmospheres at 490 °C where the carbonate is in a molten state. The bands at 1072 cm<sup>-1</sup>, 790 cm<sup>-1</sup> and 885 cm<sup>-1</sup>, 707 cm<sup>-1</sup>, 1391 cm<sup>-1</sup> and 1421 cm<sup>-1</sup>, 1762 cm<sup>-1</sup> shown in Fig. 4(a) recorded in a N<sub>2</sub> atmosphere correspond to the symmetric stretching ( $\nu_1$ ), out-of-plane bending ( $\nu_2$ ), in-plane bending ( $\nu_4$ ), asymmetric stretching ( $\nu_3$ ), and the overtone of the out-of-plane

bending mode ( $2\nu_2$ ) vibrations, respectively. The Raman spectrum in air is almost identical to that collected in N<sub>2</sub>. However, the peaks at 1317 cm<sup>-1</sup> and 1582 cm<sup>-1</sup> shown in Fig. 3(c) are only observable in the CO<sub>2</sub> atmosphere. The strong CO<sub>2</sub>-dependence of the bands at 1317 cm<sup>-1</sup> and 1582 cm<sup>-1</sup> provides a crucial hint to the formation of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> via the CO<sub>2</sub> chemisorption reaction of eqn (3).

The theoretical support to the formation of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> is provided by the DFT calculations. The calculations indicate that high Raman activities of C<sub>2</sub>O<sub>5</sub><sup>2-</sup> are within a band width of 1200–1600 cm<sup>-1</sup>. Specifically, the active Raman bands are predicted at 1366 cm<sup>-1</sup>, 1531 cm<sup>-1</sup> and 1566 cm<sup>-1</sup> for Li<sub>2</sub>C<sub>2</sub>O<sub>5</sub> and 1345 cm<sup>-1</sup>, 1547 cm<sup>-1</sup> and 1579 cm<sup>-1</sup> for Na<sub>2</sub>C<sub>2</sub>O<sub>5</sub>, respectively. The recorded spectrum in the band width of 1200–1650 cm<sup>-1</sup> from the MC within 490–525 °C in a CO<sub>2</sub> atmosphere could, therefore, be an overlap of these characteristic Raman peaks of Li<sub>2</sub>C<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>5</sub> in this band region. To deconvolute the two unique broad peaks at around 1317 cm<sup>-1</sup> and 1582 cm<sup>-1</sup>, we used Gaussian–Lorentzian function with the six theoretical Raman frequencies as the standards. The results are shown in Fig. 5, where the black and red lines represent the measured and modeled spectra, respectively. Also shown is the individual spectrum calculated for the pure Li<sub>2</sub>C<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>5</sub>, represented by pink and blue lines, respectively. It appears that the modeled spectrum is dominated by the Na<sub>2</sub>CO<sub>3</sub>; only one peak at 1566 cm<sup>-1</sup> is visible for the Li<sub>2</sub>CO<sub>3</sub> while the other two are too weak to be seen. This is primarily due to the differences in size and polarizability of the Na<sup>+</sup> and Li<sup>+</sup> ions. Overall, the measured Raman spectrum is in excellent agreement with the DFT calculations if the temperature effect is factored in. To further experimentally verify the C<sub>2</sub>O<sub>5</sub><sup>2-</sup>-centered Pathway-2 mechanism, we will measure in a future study the CO<sub>2</sub> permeation flux through a permeation cell with the feed-side surface covered by a layer of MC, where only 2PBs are available for the Pathway-2 mechanism.

**Fig. 4** Raman spectra of the molten (Li/Na)<sub>2</sub>CO<sub>3</sub> measured as a function of atmosphere at 525 °C.**Fig. 5** Deconvolution of the two broad bands observed at 1317 cm<sup>-1</sup> and 1582 cm<sup>-1</sup>; inset: the measured and DFT-modeled Raman spectra in a band width of 1200–1650 cm<sup>-1</sup>.

## Conclusion

In summary, we demonstrate the first experimental evidence for the existence of pyrocarbonate  $\text{C}_2\text{O}_5^{2-}$  species in a eutectic  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$  melt exposed to a  $\text{CO}_2$  atmosphere through a combined “DFT modeling” and “Raman spectroscopy” approach. The existence of  $\text{C}_2\text{O}_5^{2-}$  species is key support to a new bi-ionic transport model established to elucidate the fundamentals of the high-flux  $\text{CO}_2$  transport phenomenon observed in the superior mixed oxide-ion and carbonate-ion conducting  $\text{CO}_2$  separation membranes. The broad Raman bands centered at  $1317\text{ cm}^{-1}$  and  $1582\text{ cm}^{-1}$  are characteristic of  $\text{C}_2\text{O}_5^{2-}$  species in molten carbonates exposed to a  $\text{CO}_2$  atmosphere. The measured characteristic Raman frequencies of  $\text{C}_2\text{O}_5^{2-}$  are in excellent agreement with the DFT-model consisting of six overlapping individual theoretical bands calculated from  $\text{Li}_2\text{C}_2\text{O}_5$  and  $\text{Na}_2\text{C}_2\text{O}_5$ .

It is important to point out that the proposed bi-ionic transport model also has implications for rational design of new multicomponent ionic conductor systems for separating and detecting critical gases such as  $\text{H}_2$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{F}_2$ , and novel materials containing  $(\text{CO}_2)_n$  chainlike moieties for high-efficiency large-scale  $\text{CO}_2$  uptake and high-density energy storage. New solid-oxide-salt systems will be accordingly explored in the future to uncover new multicomponent heterogeneous ionic conductor systems.

## Acknowledgements

This work is supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under grant number W911NF-10-R-006.

## References

- 1 U.S. Energy Information Administration, Energy Perspective 1949–2010, October 19, 2011.
- 2 U.S. Energy Information Administration, Annual Energy Outlook 2011, April 26, 2011.
- 3 DOE/NETL, Carbon dioxide capture and storage RD&D roadmap, December 2010.
- 4 DOE/NETL, Advanced carbon dioxide capture R&D program: technology update, September 2010.
- 5 L. Zhang, N. Xu, X. Li, S. Wang, K. Huang, W. H. Harris and W. K. S. Chiu, High  $\text{CO}_2$  Permeation Flux Enabled by Highly Interconnected Three Dimensional Ionic Channels in Selective  $\text{CO}_2$  Separation Membranes, *Energy Environ. Sci.*, 2012, **5**, 8310–8317.
- 6 R. Bredeesen, K. Jordal and O. Bolland, High-temperature membranes in power generation with  $\text{CO}_2$  capture, *Chem. Eng. Process.*, 2004, **43**, 1129–1158.
- 7 B. J. P. Buhre, L. K. Elliott, C. D. Sheng, R. P. Gupta and T. F. Wall, Oxygen-fuel combustion technology for coal-fired power generation, *Prog. Energy Combust. Sci.*, 2005, **31**, 283–307.
- 8 M. O. Franklin,  $\text{CO}_2$  capture and storage: are we ready?, *Energy Environ. Sci.*, 2009, **2**, 449–458.
- 9 E. Favre, Carbon dioxide recovery from post-combustion processes: can gas permeation membranes compete with absorption?, *J. Membr. Sci.*, 2007, **294**, 50–59.
- 10 L. Bastin, P. S. Brcia, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues and B. A. Chen, Microporous metal-organic framework for separation of  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  by fixed-bed adsorption, *J. Phys. Chem. C*, 2008, **112**(5), 1575–1581.
- 11 A. M. Scurto, S. N. V. K. Aki and J. F. Brennecke,  $\text{CO}_2$  as a separation switch for ionic liquid-organic mixtures, *J. Am. Chem. Soc.*, 2002, **124**(35), 10276–10277.
- 12 A. Samanta, A. Zhao, G. K. H. Shimizu, P. Sarkar and R. Gupta, Post-combustion  $\text{CO}_2$  capture using solid sorbents: A Review, *Ind. Eng. Chem. Res.*, 2012, **51**(4), 1438–1463.
- 13 A. B. Rao and E. S. A. Rubin, Technical, Economic, and Environmental Assessment of Amine-Based  $\text{CO}_2$  Capture Technology for Power Plant Greenhouse Gas Control, *Environ. Sci. Technol.*, 2002, **36**(20), 4467–4475.
- 14 H. Kawamura, T. Yamaguchi, N. N. Balagopal, K. Nakagawa and S. Nakao, Dual-Ion Conducting Lithium Zirconate-Based Membranes for High Temperature  $\text{CO}_2$  Separation, *J. Chem. Eng. Jpn.*, 2005, **38**(5), 322–328.
- 15 E. J. Granite and T. O'Brien, Review of novel methods for carbon dioxide separation from flue and fuel gases, *Fuel Process. Technol.*, 2005, **86**, 1423–1434.
- 16 N. Du, H. B. Park, M. M. Dal-Cin and M. D. Guiver, Advances in high permeability polymeric membrane materials for  $\text{CO}_2$  separations, *Energy Environ. Sci.*, 2012, **5**, 7306–7322.
- 17 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, Advances in  $\text{CO}_2$  capture technology-the US Department of Energy's carbon sequestration program, *Int. J. Greenhouse Gas Control*, 2008, **2**, 9–20.
- 18 M. A. Carreon, S. Li, J. L. Falconer and R. D. Noble, Alumina-Supported SAPO-34 Membranes for  $\text{CO}_2/\text{CH}_4$  Separation, *J. Am. Chem. Soc.*, 2008, **130**(16), 5412–5413.
- 19 M. M. Maroto-Valer, Z. Tang and Y. Zhang,  $\text{CO}_2$  capture by activated and impregnated anthracites, *Fuel Process. Technol.*, 2005, **86**(14–15), 1487–1502.
- 20 C. Stewart and M. A. Hessami, A study of methods of carbon dioxide capture and sequestration—the sustainability of a photosynthetic bioreactor approach, *Energy Convers. Manage.*, 2005, **46**(3), 403–420.
- 21 ARPA-E Carbon Capture Programs, Taillores Post-Combustion Carbon Capture Workshop, July 11, 2010.
- 22 C. F. Hendricks, Carbon dioxide removal from coal-fired power plants, *Energy Environ.*, 1994, **1**, 19–49.
- 23 D. Shekhawal, D. R. Luebke, H. W. Pennline, A review of carbon dioxide selective membranes, National Energy Technology Laboratory, DOE/NETL, 2003.
- 24 S. Himeno, T. Tomita, K. Suzuki, K. Nakayama, K. Yajima and S. Yoshida, Synthesis and Permeation Properties of a DDR-Type Zeolite Membrane for Separation of  $\text{CO}_2/\text{CH}_4$  Gaseous Mixtures, *Ind. Eng. Chem. Res.*, 2007, **46**(21), 6989–6997.

- 25 D. Shekhawat, D. R. Luebke, H. W. A. Pennline, Review of Carbon Dioxide Selective Membranes: A Topical Report. **2003**, DOE/NETL-2003/1200.
- 26 R. Quinn, J. B. Appleby and P. G. Pez, New facilitated transport membranes for the separation of carbon dioxide from hydrogen and methane, *J. Membr. Sci.*, 1995, **104**(1–2), 139–146.
- 27 G. Moutiers, M. Gassir and J. Devynck, Oxygen reduced species in molten  $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$  (42.7 + 57.3 mol%) at 650 °C: a thermodynamic, voltammetric and convolution potential sweep characterization, *J. Electroanal. Chem.*, 1991, **324**, 175–189.
- 28 A. Borucka, Evidence for the existence of stable  $\text{CO}_2^-$  ion and response time of gas electrodes in molten alkali carbonates, *J. Electrochem. Soc.*, 1977, **124**, 972.
- 29 J. L. Wade, K. S. Lackner and A. C. West, Transport model for a high temperature, mixed conducting  $\text{CO}_2$  separation membrane, *Solid State Ionics*, 2007, **178**, 1530–1540.
- 30 M. Anderson and Y. S. Lin, Carbonate-ceramic dual-phase membrane for carbon dioxide separation, *J. Membr. Sci.*, 2010, **357**, 122–129.
- 31 J. L. Wade, C. Lee, A. C. West and K. S. Lackner, Composite electrolyte membranes for high temperature  $\text{CO}_2$  separation, *J. Membr. Sci.*, 2011, **369**, 20–29.
- 32 Z. Rui, M. Anderson, Y. Li and Y. S. Lin, Ionic conducting ceramic and carbonate dual phase membranes for carbonate dioxide separation, *J. Membr. Sci.*, 2012, **417–418**, 174–182.
- 33 N. Xu, X. Li, M. A. Franks, H. Zhao and K. Huang, Silver-molten carbonate composite as a new high-flux membrane for electrochemical separation of  $\text{CO}_2$  from flue gas, *J. Membr. Sci.*, 2012, **401–402**, 190–194.
- 34 L. Zhang, X. Li, S. Wang, K. G. Romito and K. Huang, High conductivity mixed oxide-ion and carbonate-ion conductors supported by a prefabricated porous solid-oxide matrix, *Electrochem. Commun.*, 2011, **13**, 554–557.
- 35 L. Zhang, Z. Mao, J. D. Thomason, S. Wang and K. Huang, Synthesis of a homogeneously porous solid oxide matrix with tunable porosity and pore size, *J. Am. Ceram. Soc.*, 2012, **95**, 1832–1837.
- 36 P. Claes, B. Thirion and J. Gilbert, Solubility of  $\text{CO}_2$  in the molten  $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$  (42 mol%) eutectic mixture at 800 °C, *Electrochim. Acta*, 1996, **41**, 141–146.
- 37 P. Claes, D. Moyaux and D. Peeters, Solubility and salvation of carbon dioxide in the molten  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  (43.5 : 31.5 : 25.0 mol%) eutectic mixture at 973K. I. Experimental part, *Eur. J. Inorg. Chem.*, 1999, 583–588.
- 38 P. Claes, D. Moyaux and D. Peeters, Solubility and salvation of carbon dioxide in the molten  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  (43.5 : 31.5 : 25.0 mol%) eutectic mixture at 973K. II. Theoretical part, *Eur. J. Inorg. Chem.*, 1999, 589–592.
- 39 K. P. Zeller, P. Schuler and P. Haiss, The Hidden Equilibrium in Aqueous Sodium Carbonate Solutions – Evidence for the Formation of the Dicarbonate Anion, *Eur. J. Inorg. Chem.*, 2005, 168–172.
- 40 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.
- 41 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098.
- 42 V. A. Rassalov, J. A. Pople, M. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223.
- 43 P. C. Harihan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- 44 M. M. Francel, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFree and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.
- 45 M. J. Frisch, *et al.*, *Gaussian 09, Revision B.01*, Gaussian Inc., Pittsburgh, PA, 2009.
- 46 T. Helgaker, K. Ruud, K. L. Bak, P. Jørgensen and J. Olsen, *Faraday Discuss.*, 1994, **99**, 165–180.
- 47 J. B. Bates, M. H. Brooker, A. S. Quist and G. E. Boyd, *J. Phys. Chem.*, 1972, **76**, 1565–1571.
- 48 N. Koura, S. Kohara, K. Takeuchi, S. Takahashi, L. A. Curtiss, M. Grimsditch and M.-L. Saboungi, *J. Mol. Struct.*, 1996, **382**, 163–169.
- 49 L.-J. Chen, X. Cheng, C.-J. Lin and C.-M. Huang, *Electrochim. Acta*, 2002, **47**, 1475–1480.
- 50 S. Kohara, N. Koura, Y. Idemoto, S. Takahashi, M.-L. Saboungi and L. A. Curtiss, *J. Phys. Chem. Solids*, 1998, **59**, 1477–1485.
- 51 R. L. Frost, A. Soisnard, N. Voyer, S. J. Palmer and W. N. Martens, *J. Raman Spectrosc.*, 2009, **40**, 645–649.
- 52 N. Wen and M. H. Brooker, *J. Phys. Chem.*, 1995, **99**, 359–368.
- 53 M. E. Boettcher, P.-L. Gehlken, H. Skogby and C. Reutel, *Mineral. Mag.*, 1997, **61**, 249–256.