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PAPER

First spectroscopic identification of pyrocarbonate for high CO₂ flux membranes containing highly interconnected three dimensional ionic channels

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Identification of the existence of pyrocarbonate ion C₂O₅²⁻ in molten carbonates exposed to a CO₂ atmosphere provides key support for a newly established bi-ionic transport model that explains the mechanisms of high CO₂ 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 C₂O₅²⁻ as an active species involved in the CO₂-transport process of MOCC membranes exposed to a CO₂ atmosphere. The two new broad peaks centered at 1317 cm⁻¹ and 1582 cm⁻¹ are identified as the characteristic frequencies of the C₂O₅²⁻ species. The measured characteristic Raman frequencies of C₂O₅²⁻ are in excellent agreement with the DFT-model consisting of six overlapping individual theoretical bands calculated from Li₂C₂O₅ and Na₂C₂O₅.

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Introduction

Manmade CO₂ emission through the use of fossil fuels is thought to be a major source for global warming and climate change. The stabilization of atmospheric CO₂ 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 CO₂ by capturing CO₂ at point-sources and geologically storing it. So far, three industrial combustion processes have been identified as the point-sources for carbon removal:^{1–10} 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 CO₂ 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 CO₂-capture are principally based on reversible chemical–physical sorption processes using

liquid solvents and solid sorbents as CO₂ scrubbers^{11–13} and on size-exclusion permeation using membranes as CO₂ molecular filters.^{14–19} However, as aforementioned, the solvents and sorbents based technology is cost prohibitive and energy intensive,^{20–24} and the membrane technology is susceptible to poor selectivity and incompatibility at high temperatures.^{25–28} 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 CO₂ separation membranes that are in theory exclusively permeable to CO₂ and compatible with elevated temperatures.^{5,29–33} 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). CO₂ is transported through the membrane in the form of CO₃²⁻, which is charge-compensated by a concomitant flow of O²⁻. Therefore, the MOCC membranes are more suited for pre-combustion application where the feedstock gas is a mixture of CO₂ and H₂. 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 CO₂ transport.^{5,34,35} The CO₂ permeation flux density measured from these membranes exposed to CO₂–H₂

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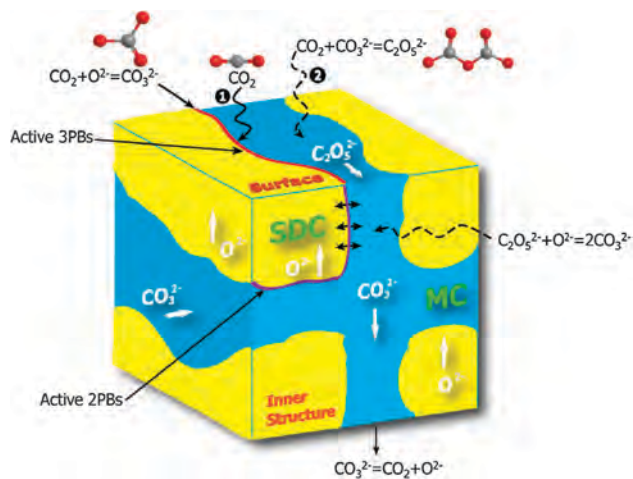
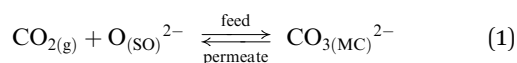


Fig. 1 A 3D-schematic illustrating electrochemical reaction occurring at 3PBs to 2PBs in dual-phase MOCC membranes; SDC = Sm₂O₃-doped CeO₂; MC = molten carbonate.

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.^{30,31}

To understand the fundamentals of a high-flux CO₂ 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 CO₂ solely at 3PBs, where CO₂, O²⁻ and CO₃²⁻ are simultaneously available at the feed surface, and subsequent transport of CO₃²⁻ through the MC phase and deionization of CO₃²⁻ on the permeate surface.



Here the subscripts (g), (SO) and (MC) represent gas, solid-oxide and molten carbonate phases, respectively. During the CO₂ transport, the flux of CO₃²⁻ is charge-compensated by the flow of O²⁻. The theoretical CO₂ flux density J_{CO_2} through 3PBs can be calculated by⁵

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

Here ε and τ are the porosity and tortuosity of the porous oxide matrix, respectively; σ_c and σ_o are ionic conductivities of the carbonate ion and the oxide ion, respectively; P'_{CO_2} and P''_{CO_2} are the partial pressure of CO₂ at the feed and permeate sides, respectively; φ 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 CO₂ ionization reaction (1) has been widely suggested in the literature as the global mechanism for CO₂

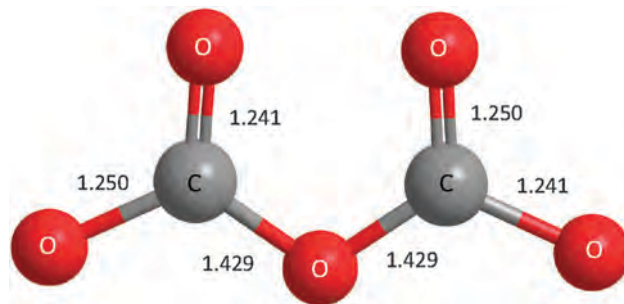
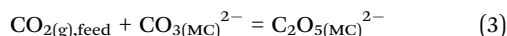


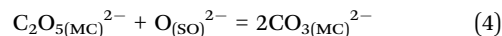
Fig. 2 Equilibrium geometry of the C₂O₅²⁻ species. The unit of bond length is in Å.

transport in dual-phase MOCC, but proceeding at a relatively slow rate.^{36–38}

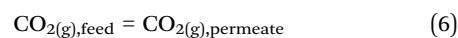
The Pathway-2 encompasses surface ionization of CO₂ at 2PBs of the CO₂/MC interface and internal ionic transfer at 2PBs of the SDC/MC interface. The species C₂O₅²⁻ (pyrocarbonate or dicarbonate anion) possessing a (CO₂)_n chainlike structure as shown in Fig. 2 is deemed an intermediate product of CO₂ chemisorption on the surface of MC *via*



Once formed, C₂O₅²⁻ can immediately react with O²⁻ available at the SDC/MC interface, dissociating into two CO₃²⁻ that can migrate to 3PBs on the permeate surface, where much faster CO₃²⁻ deionization reaction takes place to release CO₂ and O²⁻.



The overall reaction of the CO₂-transport is, therefore, given by



Overall, the reactive zones for the CO₂-transport are extended from 3PBs to 2PBs, significantly increasing the reactive areas, thus being largely responsible for the observed high CO₂ flux. Key support to the above new bi-ionic transport model is the experimental evidence of C₂O₅²⁻ existing on the surface of a MC exposed to a CO₂ atmosphere. The likelihood of absorbing CO₂ on the surface of a MC to form C₂O₅²⁻ has been suggested by Claes *et al.*^{36–38} who studied the solubility and solvation of CO₂ in a molten eutectic mixture of Li₂CO₃-Na₂CO₃-K₂CO₃ at 973 K. They found CO₂ 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_{3(MC)}²⁻ + CO_{2(g)} = C₂O_{5(MC)}²⁻. DFT calculations were carried out by the authors to gain insight into the reaction energetics. The calculated values for ΔH^0 and ΔG^0 are -223 kJ mol⁻¹ and -119 kJ mol⁻¹ at 973K, respectively, indicating favorable gas-phase energetics, and solvation should not hinder the formation of the postulated C₂O₅²⁻ in the MC. Furthermore, another study reported cross-over ¹³C-NMR experiments between [¹³C] and [¹⁸O] carbonates

in aqueous solutions of Na_2CO_3 .³⁹ 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 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 Li_2CO_3 – Na_2CO_3 melt surrounded by a 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 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 Li_2CO_3 and Na_2CO_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 $^\circ\text{C}$). 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 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 $^\circ\text{C}$) and atmosphere (in N_2 , air, CO_2).

DFT modeling

DFT calculations were performed at the B3LYP/6-31G(d)^{40–44} level using the Gaussian09⁴⁵ 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.⁴⁶

Results and discussion

Temperature dependence of the Raman spectrum

Fig. 3(a) shows the Raman spectra collected from a eutectic Li_2CO_3 – Na_2CO_3 (52 mol% Li_2CO_3 – Na_2CO_3) melt over a band range of 650 – 1850 cm^{-1} as a function of temperature in a pure CO_2 atmosphere. For the carbonate in the solid state, the

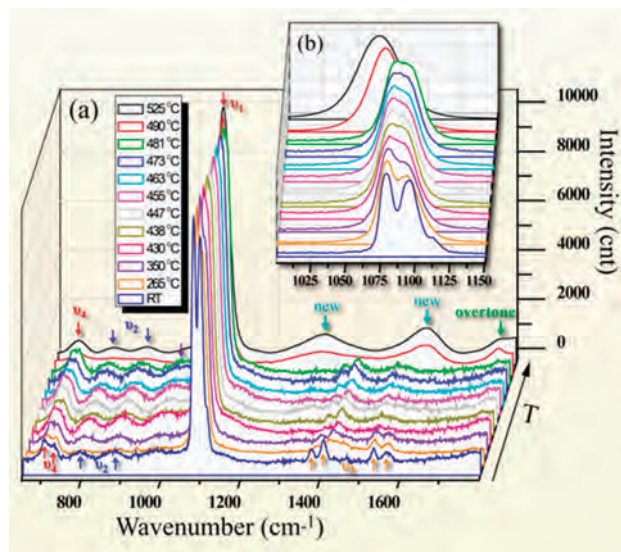


Fig. 3 (a) The Raman spectra of $(\text{Li}/\text{Na})_2\text{CO}_3$ in the region of 650 – 1850 cm^{-1} as a function of temperature in a CO_2 atmosphere; (b) magnified view in the region of 1000 – 1150 cm^{-1} .

Raman spectra are seen to contain four basic vibrational modes relevant to CO_3^{2-} ions. The two bands at 1078 and 1094 cm^{-1} are assigned to ν_1 of symmetric stretching vibrations in Li_2CO_3 and Na_2CO_3 , whereas the bands at 792 cm^{-1} and 870 cm^{-1} are assigned to ν_2 of out-of-plane bending vibrations.^{47–49} For the isolated CO_3^{2-} that has a D_{3h} symmetry, ν_2 is Raman inactive. However, it is likely that ν_2 becomes Raman active for $(\text{Li}/\text{Na})_2\text{CO}_3$ due to the distortion of the CO_3^{2-} structure imposed by the cations.⁵⁰ The observed bands at 704 and 728 cm^{-1} are assigned to ν_4 of in-plane bending vibrations. This mode is a double degeneration for the distorted CO_3^{2-} induced by Li^+ and Na^+ . As the CO_3^{2-} group becomes distorted from its regular planar symmetry, this mode splits into two components.⁵¹ The bands at 1375 cm^{-1} , 1404 cm^{-1} , 1531 cm^{-1} and 1563 cm^{-1} are attributed to a split ν_3 of the asymmetric stretching vibrations caused by the existence of Li^+ and Na^+ around the CO_3^{2-} ions.⁵⁰

The shift of the Raman band with temperature is better viewed in Fig. 3(b), a magnified spectrum showing the region of the major ν_1 -bands at 1078 cm^{-1} and 1094 cm^{-1} . As the temperature increases, the ν_1 -bands for Li_2CO_3 and Na_2CO_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.⁵² When the temperature reaches the melting point, the overtone of the out-of-plane bending mode ($2\nu_2$) appears at 1762 cm^{-1} .⁵³ It should be noted that a broad but small peak near 970 cm^{-1} only observed in solid-state carbonates appears not to be directly related to 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)₂CO₃ at selected temperatures and atmospheres

Atmospheres	CO ₂				Air	N ₂
	RT	350	455	490 (melted)	490 (melted)	490 (melted)
Temperatures (°C)	RT	350	455	490 (melted)	490 (melted)	490 (melted)
Frequencies (cm ⁻¹)	704	706	706	707	707	707
ν_4 (weak)	728	720	715	—	—	—
	792	790	789	790	790	790
ν_2 (weak)	879	879	881	882	885	885
	1078	1077	1077	1070	1072	1072
ν_1 (strong)	1094	1090	1087	—	—	—
	1375	1385	1386	—	1391	1392
	1404	1415	1416	—	1421	1421
ν_3 (weak)	1531	1520	1520	—	—	—
	1563	1555	1545	—	—	—
New peaks (broad)	—	—	—	1317	—	—
	—	—	—	1582	—	—
Overtone ($2\nu_2$)	—	—	—	1762	1762	1762
Unknown	—	—	972	—	—	—

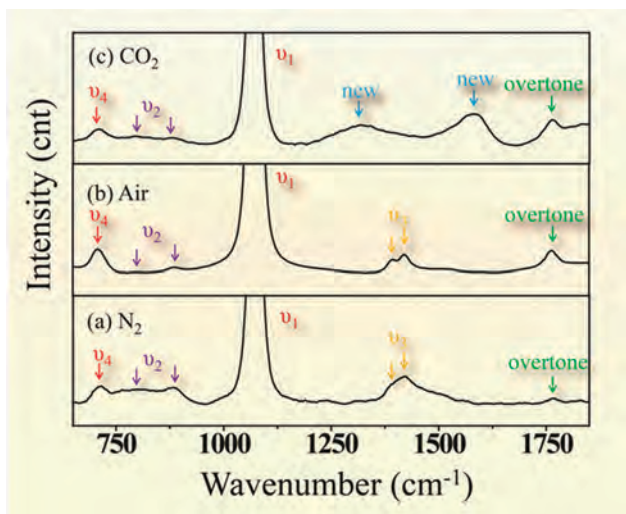
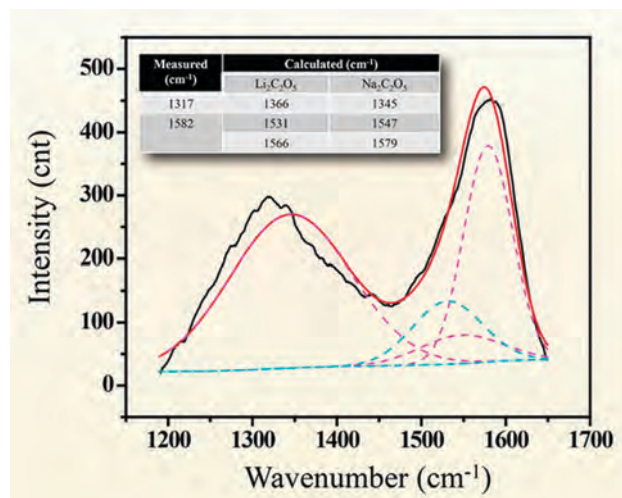
The most distinguishable features of Raman spectra in Fig. 3 are observed when the carbonate is in a molten state. The four bands corresponding to the ν_3 mode disappear from the spectrum while two new broad bands at 1317 cm⁻¹ and 1582 cm⁻¹ emerge within the same band width. A natural question to ask is: are these newly emerged Raman bands associated with the C₂O₅²⁻ 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 C₂O₅²⁻ requires a source of CO₂. Fig. 4 compares the Raman spectra measured in N₂, air and pure CO₂ atmospheres at 490 °C where the carbonate is in a molten state. The bands at 1072 cm⁻¹, 790 cm⁻¹ and 885 cm⁻¹, 707 cm⁻¹, 1391 cm⁻¹ and 1421 cm⁻¹, 1762 cm⁻¹ shown in Fig. 4(a) recorded in a N₂ atmosphere correspond to the symmetric stretching (ν_1), out-of-plane bending (ν_2), in-plane bending (ν_4), asymmetric stretching (ν_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 N₂. However, the peaks at 1317 cm⁻¹ and 1582 cm⁻¹ shown in Fig. 3(c) are only observable in the CO₂ atmosphere. The strong CO₂-dependence of the bands at 1317 cm⁻¹ and 1582 cm⁻¹ provides a crucial hint to the formation of C₂O₅²⁻ via the CO₂ chemisorption reaction of eqn (3).

The theoretical support to the formation of C₂O₅²⁻ is provided by the DFT calculations. The calculations indicate that high Raman activities of C₂O₅²⁻ are within a band width of 1200–1600 cm⁻¹. Specifically, the active Raman bands are predicted at 1366 cm⁻¹, 1531 cm⁻¹ and 1566 cm⁻¹ for Li₂C₂O₅ and 1345 cm⁻¹, 1547 cm⁻¹ and 1579 cm⁻¹ for Na₂C₂O₅, respectively. The recorded spectrum in the band width of 1200–1650 cm⁻¹ from the MC within 490–525 °C in a CO₂ atmosphere could, therefore, be an overlap of these characteristic Raman peaks of Li₂C₂O₅ and Na₂C₂O₅ in this band region. To deconvolute the two unique broad peaks at around 1317 cm⁻¹ and 1582 cm⁻¹, 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 Li₂C₂O₅ and Na₂C₂O₅, represented by pink and blue lines, respectively. It appears that the modeled spectrum is dominated by the Na₂CO₃; only one peak at 1566 cm⁻¹ is visible for the Li₂CO₃ while the other two are too weak to be seen. This is primarily due to the differences in size and polarizability of the Na⁺ and Li⁺ 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 C₂O₅²⁻-centered Pathway-2 mechanism, we will measure in a future study the CO₂ 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)₂CO₃ measured as a function of atmosphere at 525 °C.**Fig. 5** Deconvolution of the two broad bands observed at 1317 cm⁻¹ and 1582 cm⁻¹; inset: the measured and DFT-modeled Raman spectra in a band width of 1200–1650 cm⁻¹.

Conclusion

In summary, we demonstrate the first experimental evidence for the existence of pyrocarbonate $C_2O_5^{2-}$ species in a eutectic Li_2CO_3 – Na_2CO_3 melt exposed to a CO_2 atmosphere through a combined “DFT modeling” and “Raman spectroscopy” approach. The existence of $C_2O_5^{2-}$ species is key support to a new bi-ionic transport model established to elucidate the fundamentals of the high-flux CO_2 transport phenomenon observed in the superior mixed oxide-ion and carbonate-ion conducting CO_2 separation membranes. The broad Raman bands centered at 1317 cm^{-1} and 1582 cm^{-1} are characteristic of $C_2O_5^{2-}$ species in molten carbonates exposed to a CO_2 atmosphere. The measured characteristic Raman frequencies of $C_2O_5^{2-}$ are in excellent agreement with the DFT-model consisting of six overlapping individual theoretical bands calculated from $Li_2C_2O_5$ and $Na_2C_2O_5$.

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 H_2 , NO_x , SO_x , Cl_2 , Br_2 , and F_2 , and novel materials containing $(CO_2)_n$ chainlike moieties for high-efficiency large-scale 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

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