Carbon dioxide assist for non-aqueous sodium–oxygen batteries

Shyamal K. Das, Shaomao Xu, Lynden A. Archer *

School of Chemical and Biomolecular Engineering, Cornell University, NY 14853, USA

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ABSTRACT

We report a novel non-aqueous Na–air battery that utilizes a gas mixture of CO_2 and O_2. The battery exhibits a high specific energy of 6500–7000 Whkg^{-1} (based on the carbon mass) over a range of CO_2 feed compositions. The energy density achieved is higher, by 200% to 300%, than that obtained in pure oxygen. Ex-situ FTIR and XRD analysis reveal that Na_2O_2, $Na_2C_2O_4$ and Na_2CO_3 are the principal discharge products. The Na–CO_2/O_2 and Mg–CO_2/O_2 battery platforms provide a promising, new approach for CO_2 capture and generation of electrical energy.

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1. Introduction

Growing interest in electrochemical energy storage for transportation and grid storage has resulted in an intensive search for alternative energy storage technologies that offer specific energies above those achievable (~200 Whkg^{-1}) with state-of-the-art lithium-ion batteries. More than a decade of research into such storage platforms has helped define the magnitude of the challenges that must be overcome for lithium-ion batteries to achieve specific energies in the 500–700 Whkg^{-1} range [1]. In this context, metal–air batteries are gaining focus because of their exceptionally high specific energies [2,3]. Among the various metal–air batteries, the Li–air and Zn–air technologies have attracted most attention.

An air battery utilizing Na as anode is attractive because of the high earth abundance, modest cost, and relatively high electrode potential (-2.71 V vs SHE) that may be achieved. Coupled with O_2, Na has the ability to deliver a specific energy of 1600 Whkg^{-1} ($2Na^+ + O_2 + 2e^- \rightarrow Na_2O_2$ at 2.33 V; estimated based on the weight of both Na and O_2 consumed). Until 2011, the potential of the Na–O_2 couple remained less explored, in comparison to the Li–O_2 battery. A report by Peled et al. demonstrated a Na–O_2 cell based on liquid Na in combination with polymer electrolytes and operated at 100 °C [4]. Fu et al. proposed an alternative Na–O_2 cell configuration that operates at room temperature in ethylene carbonate/dimethyl carbonate as electrolyte [5]. They reported a stable discharge plateau at 2.3 V, corresponding to Na_2O_2 formation.

CO_2 is a greenhouse gas and has been implicated in global climate change [6]. A variety of chemical and physical methodologies are under development for capturing and sequestering the thousands of metric tons of the gas emitted per annum [6–8]. A metal–air battery that utilizes a mixed fuel of CO_2 and O_2 provides a potentially novel platform for electrical energy generation and carbon capture [9]. Recently, researchers at Toyota reported that incorporation of CO_2 with O_2 improves the energy density of a Li–O_2 battery [10], indicating that there may be other benefits for incorporating CO_2 in other metal–air batteries.

Herein, we report novel Na–CO_2/O_2 and Mg–CO_2/O_2 batteries operated at room temperature utilizing tetraglyme and an ionic liquid as electrolyte. Unlike the Li–O_2/CO_2 battery [10], which specifically aims to use CO_2 to enhance the energy density of the Li–O_2 cell, the current work focuses on metal–CO_2/O_2 batteries as platforms for CO_2 capture in a technology that also produces electrical energy. Both of these goals are met using a "primary" battery, i.e. one that removes/concentrates CO_2 from an effluent gas mixture, and therefore does not require the cathode reactions to be reversible. While the economics of such a battery based on lithium anode may be impractical, they can become viable for anodes based on a variety of earth abundant materials such as Na, Mg, Al, Zn, Ca, Cu, and Fe [11]. As with other CO_2 capture technologies, we envision metal–CO_2/O_2 batteries as the first step in a systematic program for CO_2 capture and sequestration, which ultimately uses chemical, biological, or geological approaches for CO_2 sequestration.

2. Experimental

The investigated Na–CO_2/O_2 battery configuration is similar to our recently reported Li–O_2 battery [12]. The air cathode consists of 90% Super P (TIMCAL) carbon and 10% PVDF binder. Mechanically perforated coin cells were used for electrochemical experiments. 1 M NaClO$_4$/tetraethylene glycol dimethylether and 0.75 M NaCF$_3$SO$_3$/ 1-ethyl-3-methyl imidazolium trifluromethanesulfonate (IL) were used as electrolytes. The cells were assembled in an argon-filled glove box. Required concentrations of CO_2 and O_2 were premixed in a chamber at 1 atm before introducing the gas feed into the battery chamber. Galvanostatic experiments were performed at 25 °C and at

a current density of 70 mAg^{-1}. The porous carbon electrode dimension is 1.95 cm^2 with typical carbon loading of 0.76–1.28 mg cm^{-2} and thickness of 5 μm. AC impedance measurements were conducted at frequencies from 100 kHz to 100 mHz at 10 mV bias voltage. Ex-situ TEM, FTIR and XRD analyses used discharged electrodes that were vacuum dried.

3. Results and discussion

Fig. 1 reports the galvanostatic discharge profiles of Na–CO$_2$/O$_2$ cells operated under various concentrations of O$_2$ and CO$_2$. Fig. 1A and B correspond, respectively, to cells using ionic liquid and tetraglyme-based electrolytes. Under a 100% O$_2$ environment, the two varieties of Na–air cells exhibit discharge capacities of 1315 mAhg^{-1} and 1390 mAhg^{-1}, respectively (estimated based on carbon mass). Unlike Fu et al. [5], the discharge profiles with pure O$_2$ feed show a less well-defined voltage plateau at 2.3 V. This difference might be attributed to the electrolytes and air cathode employed in our studies, since the current rates are similar [12]. The Na–CO$_2$/O$_2$ cells also show low discharge capacities of 183 and 173 mAhg^{-1} under pure CO$_2$ environment. Sluggish reaction kinetics between Na$^+$ ions and CO$_2$ at room temperature is anticipated [9], which may explain the latter observation. Remarkably, the discharge capacities of both the IL and tetraglyme based Na–CO$_2$/O$_2$ cells based on feed streams containing 40% and 63% CO$_2$ are respectively 3500 and 2882 mAhg^{-1}; an increase of 2.6 and 2.1 times compared to the

Na-100% O$_2$ case. Fig. 1C reports the relative discharge capacities as a function of CO$_2$ concentration. The variation in capacity depends on the chemical composition of the electrolytes, but displays a similar trend for the tetraglyme- and IL-based electrolytes, with the highest discharge capacities observed at intermediate CO$_2$ compositions. It demonstrates that the specific energy of a Na–air cell can be significantly enhanced, by factors of 2 to 3, by introducing optimized concentrations of CO$_2$. It is also apparent that the optimal ratio of CO$_2$/O$_2$ for the largest discharge capacity lies between 40% and 70% CO$_2$ and depends on the composition of the electrolyte. The optimal CO$_2$/O$_2$ feed composition is also expected to be a function of temperature [12].

It is also apparent from Fig. 1A and B that irrespective of electrolyte, there is an improvement in the quality of the discharge voltage profile upon introduction of CO$_2$ to the cells. A plateau voltage around 2–2.2 V is observed in both cases. Fig. 1D shows discharge profiles obtained from two identical tetraglyme-based Na–air cells operated under O$_2$ (37%)/CO$_2$ (63%) concentrations. A polarization of ~500 mV is observed between the cells. To understand the origin of this effect, two identical Na–air cells were assembled and stored separately in Ar and O$_2$/CO$_2$ environments. AC impedance spectra of the cells were measured at various time periods at open circuit conditions as shown in Fig. 1E and F. The results for the Ar-stored Na–air cell suggest that the electrolyte in contact with reactive Na metal forms a stable electrode/electrolyte interface over time. It is also evident from the figure that the Na–air cell stored in O$_2$/CO$_2$ exhibits less interfacial stability. As
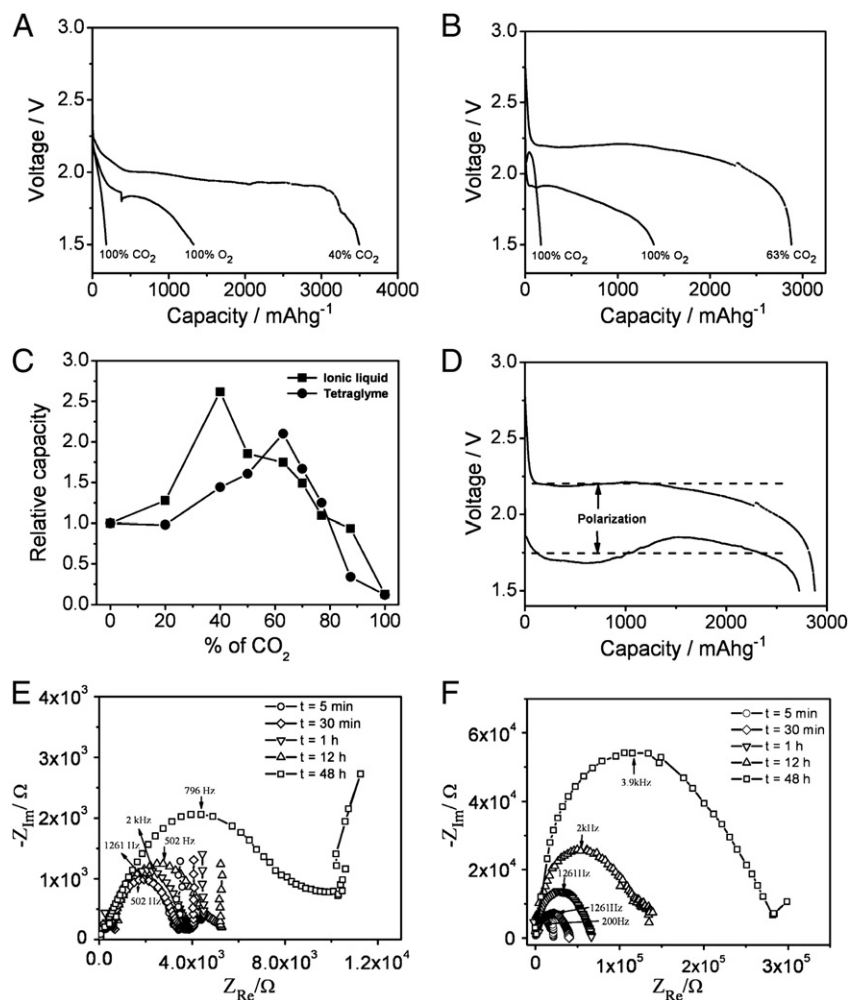

Fig. 1. Galvanostatic discharge profiles for Na–CO$_2$/O$_2$ cells operated with a mixed O$_2$/CO$_2$ feed. (A) Ionic liquid (IL) and (B) tetraglyme electrolytes; (C) variation of capacity with CO$_2$ concentration; (D) discharge profile for tetraglyme-based Na–CO$_2$/O$_2$ cells with a O$_2$ (37%)/CO$_2$ (63%) feed; AC impedance spectra of Na–air cells at open circuit under: (E) Ar and (F) O$_2$/CO$_2$ atmospheres.

the Na and carbon electrodes were separated by a micrometer thick separator and no gas protective layer covers the Na anode, it is anticipated that O_2/CO_2 diffuse and react with Na and the reaction products induce an increase in interfacial resistance at the electrode/electrolyte interface. Because a thicker electrode/electrolyte interface is anticipated for the cells stored in the O_2/CO_2 environment, more energy is required for the electrochemically generated Na^+ ions to migrate to the cathode oxidant, which would cause the observed cell polarization.

To obtain deeper insights into the overall electrochemistry and role of CO_2 the discharged carbon electrodes were harvested and investigated by TEM, XRD, and FTIR spectroscopy. Ex-situ TEM images (Fig. 2B and C), indicate that the porous carbon electrodes are filled with discharge products. Fig. 2D shows that additional X-ray diffraction peaks emerge in every case (Fig. 2Db–d). The peaks can be indexed to crystalline phase of Na_2O_2 (ICDD no. 083-0597) in case of Na-100% O_2 cells (Fig. 2D). Remarkably, however, no signature of

Na_2O_2 is found in electrodes from the O_2/CO_2 mixed gas feed. Instead, diffraction peaks for Na_2CO_3 (ICDD no. 075-6816) and $Na_2C_2O_4$ (ICDD no. 075-3639) are observed. Additionally, while Na_2CO_3 and $Na_2C_2O_4$ coexist for the tetraglyme based Na–O_2/CO_2 cells (Fig. 2Dd), $Na_2C_2O_4$ is the dominant phase for cells using the IL electrolyte (Fig. 2D). Ex-situ FTIR supports these observations (Fig. 2E and F). Peaks at 1652 cm^{-1} and 877 cm^{-1} (Fig. 2Ec and Fc, $) can be assigned to Na_2O_2 [13]. Peaks at 1632 cm^{-1} and 775 cm^{-1} (Fig. 2Ed, #) respectively correspond to antisymmetric stretching and in plane modes of O–C–O in oxalates. IR peaks at 1426 cm^{-1} and 879 cm^{-1} (Fig. 2Fd, *) correspond to O–C≡O vibrations in carbonates.

The XRD and FTIR results suggest that the following electrochemical reaction may occur in cells that employ pure O_2: $O_2 + 2e^- + 2Na^+ \rightarrow Na_2O_2$ [5]. The processes by which Na_2CO_3 and $Na_2C_2O_4$ are formed for O_2/CO_2 mixed gas feed are likely more complex. Electrochemical reduction of O_2 and CO_2 is known to involve complicated
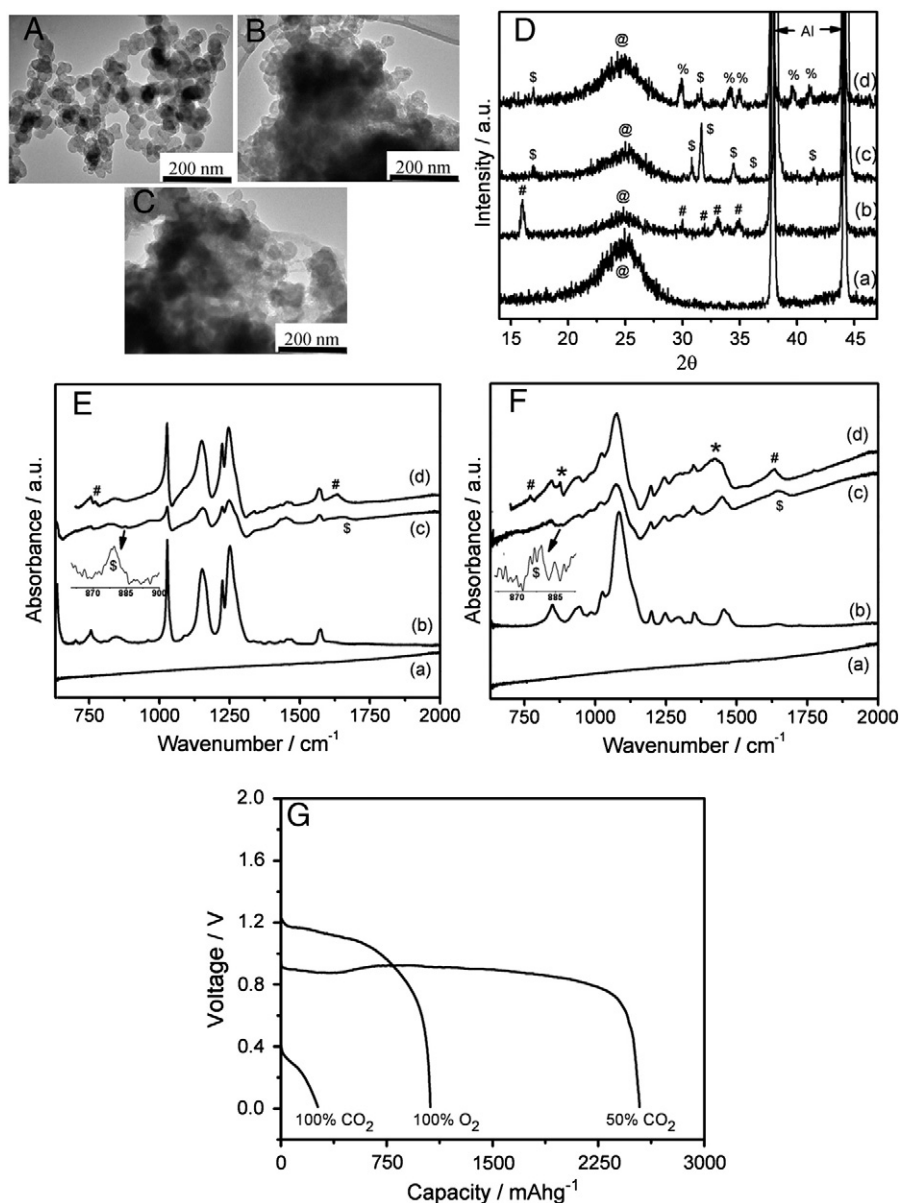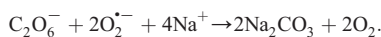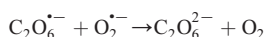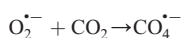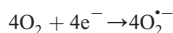

Fig. 2. Ex-situ TEM micrographs of Super P carbon (A), discharged carbon electrodes harvested from IL (B) and tetraglyme (C) cells; (D) Ex-situ XRD of Super P electrode (a), and electrodes obtained from Na–O_2 IL cell (b), Na–CO_2/O_2 IL cell (c) and Na–CO_2/O_2 tetraglyme cell (d); @, #, $, and % denote graphitic carbon, Na_2O_2, $Na_2C_2O_4$, and Na_2CO_3 phases respectively. Ex-situ FTIR spectra for Super P carbon (Ea, Fa), IL electrolyte (Eb), tetraglyme electrolyte (Fb), discharged carbon electrodes harvested from: Na–O_2 cells based on IL (Ec) and tetraglyme (Fc), Na–CO_2/O_2 cells based on IL (Ed) and tetraglyme (Fd). $, #, and * denote vibrations from Na_2O_2, $Na_2C_2O_4$, and Na_2CO_3 respectively. (G) Galvanostatic discharge curves for Mg–air cells.

elementary reactions and also depends on the solvent and electrode material [14,15]. It should be noted nonetheless that the fact that only $Na_2C_2O_4$ forms in IL based electrolytes, whereas both Na_2CO_3 and $Na_2C_2O_4$ coexist in tetraglyme cells indicates that the reactions are not hopelessly complex. Various research groups have reported on the electrochemical reduction of O_2 and CO_2 [14,15]. Based on the reported results and the observations above, we propose the following preliminary view of the reaction mechanisms for the Na–O_2/CO_2 cell.

Mechanism 1 [10,13]:

$$4O_2 + 4e^- \rightarrow 4O_2^{\bullet-}$$

$$O_2^{\bullet-} + CO_2 \rightarrow CO_4^{\bullet-}$$

$$CO_4^{\bullet-} + CO_2 \rightarrow C_2O_6^{\bullet-}$$

$$C_2O_6^{\bullet-} + O_2^{\bullet-} \rightarrow C_2O_6^{2-} + O_2$$

$$C_2O_6^- + 2O_2^{\bullet-} + 4Na^+ \rightarrow 2Na_2CO_3 + 2O_2.$$

Mechanism 2: The O_2 electroreduction reactions in aprotic organic solvents are as follows. (i) $O_2 + e^- \rightarrow O_2^{\bullet-}$ and (ii) $O_2 + 2 e^- \rightarrow O_2^{2-}$ [14]. Since $Na_2C_2O_4$ is a discharge product, the following reactions are also possible:

$$CO_2 + O_2^{2-} \rightarrow CO_4^{2-}$$

$$CO_4^{2-} + CO_2 + 2Na^+ \rightarrow Na_2C_2O_4 + O_2.$$
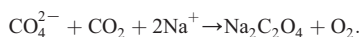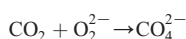
Mechanism 3: The CO_2 electroreduction reactions in aprotic organic solvents are as follows. (i) $2CO_2 + 2e^- \rightarrow C_2O_4^{2-}$ and (ii) $2CO_2 + 2e^- \rightarrow CO_3^{2-} + CO$ [15]. Since Na-100% CO_2 cells also show some capacity, a direct reaction with CO_2 must also be possible:

$$C_2O_4^{2-} + 2Na^+ \rightarrow Na_2C_2O_4 \text{ and } CO_3^{2-} + 2Na^+ \rightarrow Na_2CO_3.$$
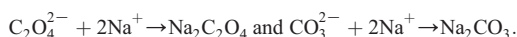
Considering a typical discharge voltage plateau at ~2 V in Na–CO_2/O_2 cells and based on the above mechanisms, it appears that mechanisms 1 and 2 are the most probable since mechanism 3 would lead to a cell voltage of ~200 mV, with mechanism 2 dominating in the IL-based electrolyte. More careful electrochemical experiments are ongoing to evaluate and refine these hypotheses.

The same ideas would lead one to expect that electrochemical properties of non-aqueous primary metal–air cells based on other earth-abundant metals, e.g. Mg, may also be enhanced by introduction of CO_2. To evaluate this idea, we assembled a Mg–air cell as a proof of concept. 1 M Mg(ClO_4)$_2$-propylene carbonate is used as electrolyte. As illustrated in Fig. 2G, the Mg–air cell shows a discharge voltage plateau of ~0.9 V and close to a factor of 250% enhancement in specific energy with introduction of 50% CO_2, underscoring its promise.

4. Conclusions

In summary, we investigated a primary non-aqueous Na–CO_2/O_2 battery as a dual platform for converting a CO_2-rich gas stream to electrical energy and for capturing the CO_2. The Na–air battery shows enhancements of 200 to 300% when a mixture of CO_2/O_2 gas with high CO_2 content is used as fuel. Preliminary postmortem structural analysis indicates that Na_2CO_3 and $Na_2C_2O_4$ are formed. We further show that metal–air batteries based on other, earth-abundant metals may also benefit from CO_2-enriched air.

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