A Molten Carbonate Membrane Enabled Liquid Gallium-CO₂ Battery for Energy Storage and CO₂ Reduction
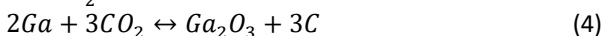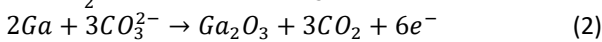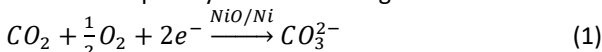
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Metal–CO₂ batteries (MCBs) are promising for simultaneous electric energy storage (EES) and CO₂ reduction (CO₂R) in utilizing renewable energies. [1] In the past decade, MCBs have been built using alkali metals (Li, Na, and K), Mg, Zn, and Al, etc. The MCBs with alkali metal anolytes typically employ nonaqueous electrolytes and produce carbon and metal carbonates by cathodic CO₂R and those of Mg, Zn and Al can operate with aqueous electrolytes to generate various carbonaceous pieces from the cathodic CO₂R. However, the electrochemical CO₂R in the MCBs involves multiple electron transfer steps with high activation energy barriers that cause kinetic limitations at low temperatures. [2] Moreover, these existing MCBs discharge resistive solids such as carbonates, oxides, and carbon at the gas(CO₂)/electrolyte/electrode triple-phase boundaries (TPBs) to hinder the mass and electric charge transfer in charging and discharging processes. [3]

In this work, a new type of high-temperature liquid gallium-CO₂ battery (LGaCB) has been established using a molten carbonate electrolyte (MCE) membrane (Fig. 1) and demonstrated to overcome the limitations of slow kinetics and inactive solid blockage of electrodes associated with the existing solid metal MCBs. The membrane-electrode assembly (MEA) of this LGaCB was comprised of a layer of LGa anolyte/anode (LGaA), a molten (Li,K) carbonate electrolyte (MCE) membrane loaded in a porous alumina disc, and a NiO/Ni gas electrode (NiGE) obtained by in situ oxidation of a Ni foam in the CO₂/air feed stream. During Discharge, the cathodic reduction of O₂/CO₂ to CO_3^{2-} (1) takes place on the gas/NiGE/MCE TPB, and the conduction of CO_3^{2-} from NiGE to LGaA occurs by O_2^-/CO_2 mixed diffusion through the MCE; then the anodic Ga oxidation (2) occurs at the LGaA/MCE interface. The full cell electrode reaction (3) has a standard potential $E_{r,298K}^o$ = 1.72 V based on the Gibbs free energy of Ga_2O_3 formation ΔG_f^o = – 998.3 kJ/mol. [4] The CO₂ molecules discharged by reaction (2) are in direct contact with LGa that permits immediate Ga-catalyzed CO₂R to C and O₂ with the latter subsequently oxidizes Ga to give overall reaction (4). [5]

Fig. 1 Schematic showing the MEA and assebled LgaCB.

$$CO_2 + \tfrac{1}{2}O_2 + 2e^- \xrightarrow{NiO/Ni} CO_3^{2-} \qquad (1)$$
$$2Ga + 3CO_3^{2-} \rightarrow Ga_2O_3 + 3CO_2 + 6e^- \qquad (2)$$
$$2Ga + \tfrac{3}{2}O_2 \rightarrow Ga_2O_3 \qquad (3)$$
$$2Ga + 3CO_2 \leftrightarrow Ga_2O_3 + 3C \qquad (4)$$

The active MEA area was around 0.36 cm². All LGaCB operations were conducted at ~508°C, which was slightly above the melting point of the eutectic (Li₀.₆₂K₀.₃₈)₂CO₃ (Tₘ ~ 498°C) and far above the Tₘ of Ga (Tₘ~ 29.8°C). During discharge, a gas mixture of 30v.% CO₂ + 70v.% air was fed into the NiGE under atmospheric pressure and a pure N₂ flow purged the LGaA side. The LGaCB was pre-activated by 8 min of supercharging at a charging current density i_{ch} of ~ 130 mA/cm² when the charging voltage V_{ch} increased from 2.4 to 3.0 V. Multiple cycles of discharge-charge operations were performed at 10 mA/cm² current density for both discharge (i_{dch}) and charge and a polarization curve was taken after the operation. The products of discharged LGa were sampled and characterized by SEM/EDS, Raman, and XPS techniques for material identification and mechanistic understanding of the cell reactions. The EDS and Raman results indicated that the discharged solids in the LGa were β-Ga₂O₃ and graphite carbon (data not shown).

The SEM image of the discharged LGa sample (Fig. 2a) revealed solids products including large carbon particles (> 50 μm) and nanosized Ga oxide needles and spheres with dia. <20 nm (insert). The Ga 2p XPS spectra (Fig. 2b) of fresh, discharged, and recharged LGa samples exhibited significant shifts of binding energy from 1115.5 and 1145 eV towards of 1120.5 and 1147 eV, respectively, after discharging, and reverse shifts back to lower energy levels after recharging. These confirmed that the redox cycle of $Ga \rightleftharpoons Ga^{3+}$ enabled the discharge and charge processes. Such electrochemical reduction of Ga oxides formed by reaction with CO₂ at high temperature was also reported in the literature. [6] Fig. 3c presents a typical discharge-charge cycle at i_{dch} and i_{ch} of 10 mA/cm², where the LGaCB achieved a power density P_e (=$V_{dch} \cdot i_{dch}$) of 12.8 mW/cm² with at an average discharge voltage of V_{dch} = 1.28 V, a ΔV_{gap} ~ 0.45 V, and a round-trip
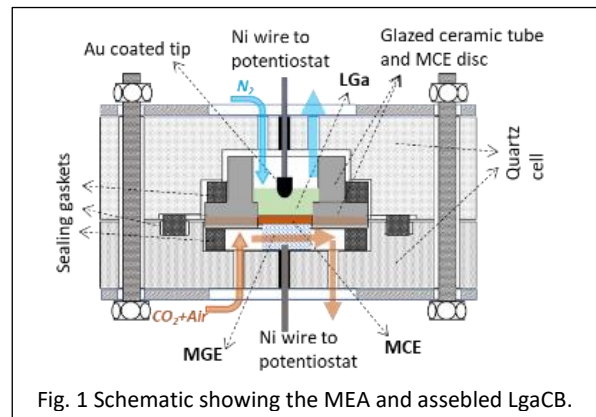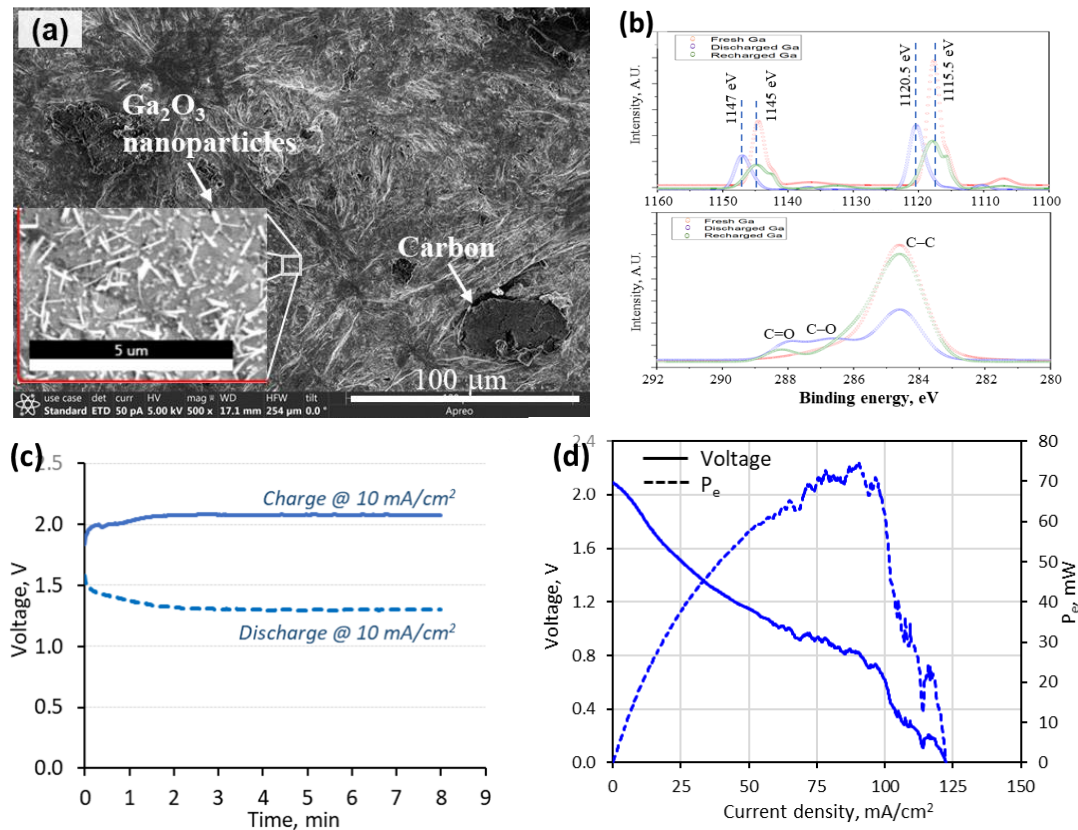
voltage efficiency $\eta_{d/ch}$ (=V_{dch}/V_{ch}) of ~ 74%. The polarization curve demonstrated a maximum P_e of ~75 mW/cm^2, which was by far the highest reported to date. [7]

Fig. 2 Products of LGaCB operation: (a) SEM images of the discharged products in LGa (insert showing needle-shaped and spherical Ga$_2$O$_3$ nanoparticles), (b) Ga 2p XPS spectra of fresh, discharged, and recharged Ga samples, (c) a charge-discharge cycle at i_{dch} and i_{ch} of 10 mA/cm^2, and (d) discharge polarization curve and P$_e$ dependency on i_{dch}.

In summary, a rechargeable high temperature LGaCB was demonstrated to overcome the limitations of slow reaction kinetics and solid blockage of gas electrode associated with the existing low temperature MCBs. During discharge of the LGaCB, CO_3^{2-} ions were generated from the CO$_2$/air feed at TPBs on NiGE and conducted through the MCE most likely via the O_2^- and CO$_2$ mixed diffusion; the LGa was then oxidized by CO_3^{2-} at the LGaA/MCE interface to complete the cell operation. Ga$_2$O$_3$ nanoparticles (dia. ~ 20 nm) and graphite large particles (>50μm) were discharged in LGaA that avoided blockage of the NiGE. In the charging process, Ga^{3+} was reduced to Ga without total oxidation of the discharged carbon that led to a carbon-negative effect from the cyclic operation. The preliminary LGaCB achieved a power density far greater than any of the reported MCBs. The findings of this work could open up opportunities for developing new liquid metal-CO$_2$ batteries to achieve practical performance for simultaneous EES and CO$_2$RC with carbon-negative effects.

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