

Continuous power supply from a baseload renewable power plant



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HIGHLIGHTS

- We propose chemical-refrigeration cycles for energy storage.
- Closed cycle between liquid CO₂ and liquid carbon fuel.
- Exergy metrics proposed to identify favorable candidate fuels.
- Methane and methanol balance storage efficiency and volumes.

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ABSTRACT

A grand challenge for using intermittent renewable energy such as solar for baseload applications is large-scale energy storage. Here, we propose an efficient means of implementing carbon recirculation cycles that enable dense energy storage. In these cycles, during the period of renewable energy availability, a suitable carbon molecule is synthesized from the stored liquid carbon dioxide and then stored in a liquid state. Subsequently, when renewable energy is unavailable, the carbon molecule is oxidized to deliver electricity and carbon dioxide is recovered and liquefied for storage. We introduce exergy based metrics to systematically identify candidate carbon molecules for the cycle. Such a search provides us the trade-off between the exergy stored per carbon atom, exergy used to synthesize the molecule and the exergy stored per unit volume. While no carbon molecule simultaneously has the most favorable values for all three metrics, favorable candidates identified include methane, methanol, propane, ethane and dimethyl ether. For cases where the molecule to be stored is gaseous under ambient conditions, we suggest synergistic integration between liquefaction and boilup of this gas and that of recirculating carbon dioxide. This unique feature allows for minimizing the energy penalty associated with the recovery, purification and liquefaction of carbon dioxide and storage of carbon molecules. Using process simulations we show that these cycles have a potential to provide GWh of electricity corresponding to an overall energy storage efficiency of 55–58% at much reduced storage volumes compared to other options.

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1. Introduction

Energy storage at multiple time and energy scales remains an on-going challenge for transitioning from fossil fuels to intermittently available renewable energy sources as the dominant primary energy supply. The impact of energy storage technologies in enabling the use of renewable energy sources like solar, wind etc. for different end uses is illustrated from the magnitude of energy to be stored. For example, in the USA, on average, solar energy is available for only one-fifth of a twenty-four hour day [1]. This means for an average 100 MW power supply from solar energy, one needs to store enough energy to supply ~2 GWh of electricity for a twenty-four hour cycle. This motivates the need to identify

methods for storing GWh levels of energy in a reasonable volume, which can also be subsequently delivered at a high efficiency. Here, we propose a GWh-level electrical energy storage system that is dense, energy efficient and makes use of carbon fuels and their existing infrastructure.

Among the known energy storage methods, current batteries are known for their high storage efficiency (75–94%) [2]. However, their currently low energy densities (<2 GJ/m³) [2,3] and short cycle life (e.g. ~2500 for sodium–sulfur batteries) [3], make them impractical for storing GWh levels of electricity. For example, commercially available sodium–sulfur batteries are typically installed to store electrical energy amounts at the MW h level, with a current world wide deployment of ~270 MW [3,4]. Use of hydrogen either as a cryogenic liquid or compressed gas results in low energy storage efficiencies typically near ~20–30% [5] (Supporting Information, SI). Use of thermophysical materials like molten salts to

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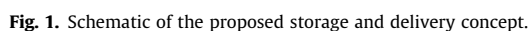
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Carbon fuels (such as alkanes, alcohols, and ethers) offer an attractive storage solution owing to their high volumetric energy density (e.g. gasoline is $\sim 32 \text{ GJ/m}^3$), efficient conversion to electricity (50–70%) [10], and the well-established technology and infrastructure available for their utilization [11,12]. Candidate fuel molecules suggested for energy storage applications include gaseous methane [12–14], methanol [5,15], dimethyl ether [14,15], and diesel [16]. However, the long-term use of such fuels for energy storage is contingent on our ability to synthesize them from renewable carbon and hydrogen sources. While hydrogen can be generated from water, the use of atmospheric carbon dioxide or biomass as possible renewable carbon source in such an open loop fashion is quite challenging [11,16,17]. For example, carbon dioxide extraction from the atmosphere, or even from industrial exhausts, is an energy intensive process, which could substantially impact the storage efficiency [12,18]. On the other hand, growing biomass on agricultural land for energy use is generally constrained by the available arable land as well as other environmental issues [8,19]. Only the Sustainably Available (SA) biomass comprising of crop residues and perennial grasses grown on marginal lands are readily available for energy production [20,21]. However, the specific availability of the limited SA biomass for energy storage is uncertain mainly due to its anticipated competitive use for synthesizing chemicals as well as liquid fuels for transportation [22]. Previous works have suggested closed loop storage cycles where the carbon dioxide formed during power generation is recirculated within the process [13,23,24]. This is consistent with the cyclical nature of energy storage and warrants further analysis to identify efficient and dense storage cycles.

they need to be either stored as liquids (close to ambient pressure) or as high-pressure gases (at ambient temperature or lower). Although liquefaction of these carbon fuels significantly reduces the storage volume, it is associated with a relatively large refrigeration energy penalty that could adversely impact the storage efficiency. High-pressure gas storage, on the other hand, is associated with a lower energy penalty, but requires much larger volumes for storing the same quantity of energy compared to liquefaction. For example, consider the large-scale storage of natural gas. A Liquefied Natural Gas (LNG) tank (~ 111 K and ~ 1.1 bar) with a typical capacity of $100,000 \text{ m}^3$ [25], is estimated to have an energy storage capability of ~ 585 GWh in terms of Lower Heating Value (LHV) (assuming NG is 100% methane). On the other hand, the state of the art compressed natural gas VOLANDS® storage tank (comprising of bundles of cylinders operating at sub-ambient temperature of ~ 243 K and ~ 125 bar) is available for a storage capacity of up to $\sim 64,000 \text{ m}^3$. This volume corresponds to a storage capability of ~ 132 GWh on a LHV basis [26]. In the USA, ~ 4 million m^3 of LNG, which is equivalent to ~ 23 TW h (LHV), is stored for NG peak demand supply [27]. Thus, as evident from the current NG storage practices, the volumetric and related practical constraints of storing large quantities of compressed gas make it less favorable compared to liquefied gas storage.

We propose the concept shown in Fig. 1, which can achieve efficient and dense energy storage using a closed carbon recirculation system. The cycle transforms carbon atoms back and forth between liquid carbon dioxide and liquid carbon fuel to enable the storage and then delivery of GWh levels of electrical energy. When renewable energy becomes available, the stored liquid carbon dioxide is vaporized and reacted with hydrogen (provided by water dissociation), to synthesize a carbon fuel. The synthesized carbon fuel is liquefied and stored. This section of the process is referred in this article as “storage mode”

To meet the power demand in absence of the renewable energy source, the stored carbon fuel is vaporized and oxidized. The oxidation by-product, carbon dioxide, goes through Capture, Purification, and Liquefaction (CPL) processes prior to storage. This part of the process is referred as the “delivery mode”. Although not essential, the water produced during the carbon fuel oxidation in



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