The Electrochemical Flow Capacitor: A New Concept for Rapid Energy Storage and Recovery

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Availability of grid-scale electric energy storage systems with response rates on the order of seconds plays a key role in wide implementation of renewable energy sources. Here, a new concept called the electrochemical flow capacitor (EFC) is presented. This new concept shares the major advantages of both supercapacitors and flow batteries, providing rapid charging/discharging while enabling the decoupling of the power and energy ratings. Like in supercapacitors, energy is stored in the electric double layer of charged carbon particles. A flowable carbon-electrolyte mixture is employed as the active material for capacitive energy storage, and is handled in a similar fashion to flow or semi-solid batteries (i.e., for charging/discharging, it is pumped into an electrochemical cell, and for storage, it is pumped into reservoirs). This study presents the proof-of-concept of this technology and reports initial EFC performance data obtained under static and intermittent flow operations.

1. Introduction

Electrical energy storage (EES) has emerged as a key technological challenge impeding the widespread implementation of intermittent renewable energy sources such as wind and solar. Viable EES technologies are also essential for increasing grid efficiency through implementation of load-leveling and peak-shaving strategies to manage the rapid fluctuations in energy demand during the day.[1] Rapid energy recovery is also critically important to enable immediate and continuous utilization of fluctuating renewable energy sources. These critical challenges can only be met by highly efficient storage technologies that are able to quickly respond to the large and rapid fluctuations, which are inherent to electrical energy generation and demand. Despite widespread efforts and a few promising approaches, no viable EES technology exists that can efficiently manage the rapid time-shifting of energy to periods of maximum demand, at scales ranging from single-family homes to metropolitan electrical distribution installations.

Significant breakthroughs in electrical energy storage have been made within the last two decades in the fields of batteries[2] and supercapacitors.[3] However, these advances primarily address small-scale storage, such as consumer and microelectronics. Flowable electrochemical systems such as redox flow batteries (RFBs),[4] molten salt batteries (primarily Na-S),[5] or the recently reported semisolid lithium flow cell (SSFC),[6] are alternative technologies for grid-scale energy storage. Unlike traditional batteries, the unique aspect of these systems is the decoupling of energy and power ratings; such that the energy storage capacity is determined by the size of the electrolyte reservoirs, whereas the power range is dependent on the size of the electrochemical cell stack (i.e., size and quantity of individual cells) and the electrochemical processes during charge/discharge. While the decoupled power and energy storage feature allows these systems to be scaled to different energy storage applications, the major inherent issue with these technologies is that they suffer from slow charging (on the order of hours) and limited cycle lifetimes (<20 000 cycles), which hinders their widespread usage.[7]

In contrast to batteries, supercapacitors show great promise to address load-leveling, peak-shaving and grid stabilization issues as they exhibit rapid charge/discharge characteristics because energy is stored physically by ion adsorption in the electric double layer (EDL), and not through inherently slower Faradaic processes. When compared to Li-ion batteries, supercapacitors provide ~10x higher power-density, ~100x faster charge/discharge rates, and ~1000x longer lifetimes at a potentially lower cost. However, current supercapacitor technology suffers from low energy density (~20x lower than batteries) and high cost, which limits their ubiquitous implementation for smart grid applications.[8]

Here, we introduce a new dynamic energy storage concept called the “electrochemical flow capacitor” (EFC), which shows promise for use in grid-scale electrical energy storage. This concept is expected to benefit from the major advantages of both supercapacitors and flow batteries; namely the high power density and long cycle lifetime of supercapacitors and the scalable energy capacity of flow batteries. The unique
and the most basic one is shown in Figure 2. A more versatile embodiment would be a double cell-stack, closed-loop system enabling charging of uncharged and discharging of previously charged slurry at the same time. This feature is of particular importance to simultaneously respond to fast fluctuations in energy production and energy consumption, which are two inherently independent parameters. Each half-cell uses a flow field or channel to direct the flow of active material over the surface of a polarized current collector.

In this study, we present the proof-of-concept of this technology and report initial performance data obtained from a prototype EFC system. Several flowable capacitive slurry compositions are benchmarked using electrochemical characterization and rheometric techniques. Both static cell and intermittent flow operation are studied. The prototype EFC shows promising performance comparable to other emerging and existing technologies, indicating that much higher performance will be possible after system optimization.

2. Results

2.1. Design of Electrochemical Flow Capacitor (EFC) Prototype

The design of the flow capacitor cell is critically important to facilitate the flow of the capacitive slurry (i.e., mitigate clogging) and maximize system performance. In particular, the flow cell design is highly dependent on the properties of the slurry used aspect of this new concept is the use of a flowable carbon-electrolyte slurry for capacitive energy storage. Fundamentally, the EFC is based on the same charge storage mechanism as supercapacitors, where reversible polarization leads to the formation of the EDL by counterbalancing the surface charges of porous electrodes (Figure 1). As such, the operation of an EFC occurs in a way that uncharged slurry (in this case, a flowable mixture of porous carbon particles with aqueous or organic electrolyte similar to the ‘slurry electrode’ introduced by KasTenig et al.\cite{9}) is pumped through a polarized flow cell, where energy storage occurs through the formation of the EDL at the surface of the carbon particles. Positively charged solid particles in the slurry attract negatively charged ions for charge balancing (and vice versa). Ion diffusion from one slurry electrode to another occurs through an ion-permeable membrane that acts as an electrical insulator (Figure 1). Once charged, the slurry is pumped into an external reservoir for storage and when it is necessary to recover the stored energy, the charged slurry is again pumped through a flow cell (Figure 2). Charging can occur very rapidly, yet power output and energy storage are decoupled, which enables energy capacity, overcoming the major limitation of supercapacitors: the moderate amount of stored energy.

At a system level, EFCs utilize an architecture similar to that found in flow batteries.\cite{6} The system consists of an electrochemical flow cell for charging and/or discharging, which is connected to an external circulatory system of pumps and reservoirs. Various conceptual designs of the EFC are possible.
for capacitive storage. Several designs were considered, tested, and evaluated before selecting the reported cell design (Figure 2). The chosen cell design provided the high level of flow control required for prototype benchmarking and also enabled testing of operation modes similar to the ones which are anticipated to be encountered for a large scale EFC device. In the selected design, a single flow channel with a depth of 1.6 mm ran through each half-cell, similar to the cell described in reference [6]. Half-cells consisted of a stainless steel current collector recessed in a polytetrafluoroethylene (PTFE) flow manifold. Polymer membranes typically used in supercapacitors and batteries were used as the isolative separator between the two half-cells. Valves with a cross-sectional diameter similar to the flow channel were installed at the inlet and outlet of the cell to minimize clogging and provide physical/electrical confinement of the slurry within the cell.

2.2. Carbon Slurry Composition

The composition of the carbon slurry determines its rheological and electrochemical properties. In particular, the concentration of carbon particles, particle size/shape, and carrier-fluid (electrolyte) viscosity have a significant effect on the performance of the carbon slurry, and can be altered to obtain improvements in rheological and electrochemical properties for enhanced slurry flow and EFC performance. In this study, carbon slurries based on spherical porous carbons with a high surface area were tested. In a suspension, spherical carbon beads with a narrow particle size distribution provide rheological advantages, minimizing the flow-induced particle size segregation and clogging such that a smooth flow pattern can be achieved. We have tested phenolic-resin-derived activated carbon beads with average particle sizes of 161 μm (CB01), 315 μm (CB03), and 383 μm (CB02; see also Supporting Information (SI)) and non-spherical carbide-derived carbon powder obtained from a titanium carbide precursor (TiC-CDC; average particle size ~2 μm). Slurries of these porous carbons were prepared with 1 M Na₂SO₄ in water and 1.25 M TEA-BF₄ in propylene carbonate (PC). Microparticulate TiC-CDC was analyzed to enable comparison of the tested slurries against a material with a high intrinsic capacitance. X-ray microtomography shows that for a 3:1 mixture (electrolyte:carbon by mass) of CB01 resting in a 1 mm capillary, most carbon beads are in direct physical contact, creating a conductive 3D network (i.e., high bead connectivity) that enables electron transport within the active material. By increasing the electrolyte mass ratio from 3:1 to 4:1, the slurry was observed to exhibit improved macroscopic flowability with glycerol-like characteristics (Figure 3d). Rheological analysis indicates that with increased shear rate, a continuous decrease in the viscosity of the slurry occurs (i.e., shear-thinning) and a change in the flow characteristics of the slurry was observed (Figure 3e). A similar trend was observed for the suspension described in reference [6].

2.3. Electrochemical Flow Capacitor Performance

Slurries based on carbon beads (3:1 mixture) and CDC (6:1 mixture) showed pronounced capacitive behavior when charged to 0.6 V in 1 M Na₂SO₄ (aqueous electrolyte) (Figure 4a) and 2.7 V in 1.25 M TEA-BF₄ in PC (organic electrolyte) using a static laboratory cell. The organic electrolyte exhibited a lower specific capacitance for CB01 (44 F/g at 2 mV/s) when compared to the performance of CB01 in aqueous electrolyte (95 F/g at 2 mV/s; Figure 4b). TiC-CDC in aqueous electrolyte demonstrated the highest capacitance with 109 F/g at 2 mV/s, while the CB03 beads demonstrated the lowest capacitance (69 F/g) under the same conditions. The measured specific capacitance of the carbon slurries translates into an energy density of approximately 0.3 Wh/liter for the aqueous carbon slurries (e.g., comparable to the potential energy of water at 100 m height difference used for hydropower) and 3.7 Wh/liter of the PC-based carbon slurry, close to the values for commercial packed supercapacitor cells. Since the carbon weight accounts for about 30% of the total mass of the packaged commercial supercapacitors, a factor of 3–4 is
Electrochemical performance of aqueous and organic carbon slurries in a static laboratory cell. Carbon beads and TiC-CDC slurries (in 1 M Na₂SO₄) charged to 0.6 V at 2 mV/s show capacitive behavior as demonstrated by rectangular CVs (a). Dependency of the specific capacitance on the charge/discharge rate in aqueous and organic electrolytes (b). Galvanostatic charge/discharge (100 mA/g) of CB01 in 1 M Na₂SO₄ shows an ohmic drop of 4.2 Ω cm² with no electrochemical side-reactions (c), facilitating a high coulombic efficiency of approximately 99% over 2,250 charge and discharge cycles (d). Open circuit voltage of a 3:1 CB01 slurry after charging to 0.75 V in 1 M Na₂SO₄ and to 2.7 V in 1.25 M TEA-BF₄ in PC for 20 min, respectively, shows faster voltage loss over time for the aqueous than for the organic electrolyte (e). Chronoamperometry shows an equilibrium capacitance of 49 F/g for CB01 tested in organic electrolyte and a high coulombic efficiency of >98% when charged to a cell potential of 2.7 V and subsequently discharged to 0 V.

In terms of specific capacitance, both cyclic voltammetry and galvanostatic charge/discharge yield a specific capacitance which is rate-dependent (i.e., depends on scan rate or current density). This can be attributed to the dynamic effects associated with transport resistance inside micro- and mesopores of the carbon particles, and across the separator. As found by chronoamperometry (Figure 4f), the intrinsic equilibrium capacitance of CB01 (aqueous: 125 F/g; organic: 49 F/g) is comparable, yet higher than the capacitance derived from rate-dependent methods (aqueous: +37%; organic: +9%; see SI for more detailed discussion). When compensating for the leakage current, the coulombic efficiency (ε) of the EFC prototype was observed to be 98.5%, which is in a very good agreement with the coulombic efficiency derived from galvanostatic charge/discharge (>99%).

frequently used to extrapolate the energy/power of the device from the performance of the material. However, this extrapolation is only valid for electrodes with the thickness and weight loading similar to that of commercial electrodes using 100–200 μm of carbon film on a current collector. For an EFC, for which the mass of the current collectors, separator, and other materials is small relative to the mass of the slurry, the total energy density of the system is roughly equal to that of the slurry. Thus, even a non-optimized system shows a respectable energy density in these preliminary tests. Values of up to ~7 Wh/liter can be achieved for ionic liquid electrolytes with a 4 V stability window, assuming a moderate capacitance of ~40 F/g.

All studied carbons showed a moderate equivalent series resistance (ESR) of ~4 Ω cm² when used in a toothpaste-like flowable 3:1 mass ratio of carbon in 1 M Na₂SO₄. This value increased by a factor of 2.7 when increasing the channel depth of the flow cell from 0.8 to 1.6 mm. The rate-performance of the carbon slurries remained limited, with significant losses in specific capacitance at scan rates faster than 10 mV/s (Figure 4b). Nonetheless, even a relatively low current density of 0.35 A/g enabled 8 full galvanostatic charge and discharge cycles within a 3 minute period (2.6 cycles per minute - one cycle every 23 seconds; Figure 4c). The corresponding gravimetric capacitance from galvanostatic charge/discharge was observed to be similar to the values obtained from cyclic voltammetry (CB01: 91 F/g in aqueous and 45 F/g in organic electrolyte). Moreover, the galvanostatic cycling performance was found to be stable, with cycle efficiencies greater than 99% for the first 2250 charge/discharge cycles (Figure 4d).

The time-dependent loss of the open circuit cell potential (referred to as self-discharge) — a common phenomenon in supercapacitors — was found to be higher for aqueous slurries than for organic carbon slurries (Figure 4e). For 20 min of charging to maximum cell potential (0.75 V for aqueous and 2.7 V for organic electrolyte), the open circuit voltage dropped to 16% of the initial voltage (0.75 V) after 24 hrs for 1 M Na₂SO₄ aqueous electrolyte, but remained at a high level of 2.3 V (= 85%) for the organic electrolyte. The latter, while being a faster decay than observed in optimized commercial packed cells, is still in the range of values reported for supercapacitors. We note that charging for a longer period will further decrease the loss of potential over time, and the separate storage of the positively and negatively polarized slurries is expected to further decrease self-discharge by eliminating leakage current, which is associated with the (undesired) charge transfer across the porous separator and insulating gaskets.
In particular, play a critical role in the performance of the EFC. In order to minimize ohmic losses, it is generally advantageous to use a very shallow channel geometry, which allows free passage of the slurry without clogging. The overall length of the channel determines the charging rate and the residence time of the slurry within the cell. While a simple channel of constant cross-section was used in this study, it is foreseeable that more elaborate channel designs will yield improved system performance. In particular, multiplexing will enable large quantities of carbon slurry to be charged or discharged in parallel to accommodate the storage or recovery of large amounts of energy. In addition, it is possible to lower the contact resistance and achieve higher flow rate capability through further engineering of the current collectors.

As seen in this proof-of-concept study, the observed capacitance of carbon beads (up to 125 F/g in aqueous electrolytes) is comparable to what has been reported for activated carbons in Na₂SO₄ (∼120 F/g) or phenolic-resin-derived carbon spheres (>150 F/g). We expect a further increase in the intrinsic carbon capacitance (>200 F/g) when utilizing materials such as ordered mesoporous carbons or hydrothermally carbonized activated carbons. While the energy density—one of the most important metrics of energy storage systems—scales linearly with the capacitance, it has a quadratic dependence on the cell potential (i.e., \( E = 0.5 CV^2 \)). This means that even for a moderate capacitance, a comparatively high energy density can be reached in electrolytes, such as ionic liquids, which enable operation in a large voltage window. In addition, eutectic ionic liquid mixtures have recently been shown to enable supercapacitor usage in a very broad temperature window (−50 to +100 °C), where a grid-scale EFC may be required to operate. Non-volatility in conjunction with a wide usable voltage window makes ionic liquids a particularly attractive electrolyte for the electrochemical flow capacitor concept, especially if their production volume increases with a decrease in cost. Very low operation temperatures are not limited to ionic liquids but are also possible when employing organic electrolytes. It has been shown recently that temperatures as low as −70 °C are possible when employing spiro-(1,1′)-bipyridinium tetrafluoroborate (SBP-BF₄) in a 1:1 (vol%) mixture of acetonitrile and methyl formate which can be considered as an alternative electrolyte to ionic liquids.

It is clear that a low interparticle connectivity will negatively affect the rate-performance and the charge transfer efficiency of carbon slurries. This aspect can be addressed by optimizing the size and loading of the carbon beads, but there should be a balance of flowability (best with low solid/liquid ratios) and charge transfer efficiency (best with high solid/liquid ratios). While a narrow particle size distribution is desirable to avoid granular convection, the flowability and particle contact would both directly benefit through the use of smaller carbon beads. To date, carbon microspheres with different sizes can be obtained from various chemical syntheses. For example, spherical carbon particles with the size of a few micrometers can be obtained by hydrothermal synthesis, while submicrometer-sized mesoporous carbon spheres can be obtained by template synthesis. Pseudocapacitive carbon microspheres (≤1 μm) produced by ultrasonic spray pyrolysis have been shown to yield a very high capacitance of up to 341 F/g. Such carbon materials possess potential to improve the energy density of the...
this new concept eliminates the need for additional current collectors, that similar energy capacities should be possible. In addition, the architectural similarities between RFB and the EFC imply varying the number of active charging/discharging channels. The principle of multiplexing, the response rate can be tailored by the scan rate and normalizing it by the weight of one electrode

where \( C \) is the capacitance, \( \Delta V \) is the voltage window, \( i \) is the discharge current, \( V \) is the voltage, \( v \) is the scan rate, and \( m \) is the mass of carbon in one electrode. The factor of 2 accounts for the two electrode setup, where the charge is evenly distributed between two capacitors in series. We note that the \( y \)-axis \((F/g)\) in Figure 4a-b was calculated by dividing twice the measured current by the scan rate and normalizing it by the weight of one electrode (corresponding to \( m \), as defined above).
Galvanostatic charge/discharge was conducted at 100 mA for 0.6 V (aqueous) and 2.7 V (organic) windows, with charge times of 120 s. The series resistance was calculated from the ohmic drop observed at the start of the discharge cycle, and the capacitance was derived from the slope of the discharge curves. All values for the capacitance were normalized by the weight of the carbon material, not the total slurry mass, to enable a direct comparison with conventional supercapacitor electrodes (which are also normalized to the content of active material). The specific capacitance \( C_{sp} \) was calculated from galvanostatic cycling using Equation (2):

\[
C_{sp} = \frac{2i}{m} \left( \frac{\Delta V}{\Delta t} \right) \tag{2}
\]

where \( \Delta V/\Delta t \) is the slope of the discharge curve.

Equilibrium capacitance was extracted from chronocoulometry.[44] After a 50 min discharge period (at 0 V), the cell was charged to a certain cell potential (e.g., 2.7 V) for 5 min and then discharged to 0 V for 5 min. While the current that was measured during charging was superimposed by the leakage current of the system, integration of the discharge curve directly yielded the charge of the two-electrode setup. The capacitance was extracted from the discharge curves with Equation (3) (see also SI):

\[
C_{dV} = \frac{\frac{1}{2} \cdot \int i \cdot dt}{m} \tag{3}
\]

The EFC prototype (Figure 2b) consisted of two stainless steel current collectors recessed in PTFE flow manifolds. 6 mm diameter throughputs allowed slurry to flow into and out of the charge/discharge cell with a 38 × 6 mm² active area (per half-cell). Two 1600 μm thick PTFE gaskets provided lateral confinement of the slurry and a polyvinylidene fluoride (PVDF) membrane with a mesh width of 100 nm (Durapore; Merck Millipore, Germany) served as a separator. Six nylon screws along the length of the cell ensured sealing of the enclosed carbon slurry during charge/discharge and flow operations.

Prior to intermittent-flow testing, slurry was pumped into the EFC prototype via a syringe. The cell then underwent 20 cyclic voltammetry cycles from 0−0.75 V at 10 mV/s to precondition the slurry and to ensure that the internal pore-space was ion-accessible. The cell was then held potentiostatically at 0 V to dissipate any remaining charge, then charged potentiostatically at 0.75 V for 20 min. At the end of the charging period, the charged slurry was withdrawn from the cell using a syringe. The slurry was then returned to the cell and discharged potentiostatically at 0 V for 20 min. The resulting chronocoulometric profile was then analyzed to determine the voltage and coulombic efficiencies of the system. Voltage efficiency (\( \varepsilon_v \)) was calculated using Equation (4):

\[
\varepsilon_v = \frac{V_{\text{max}}}{V_{\text{discharge}}} \cdot 100\% \tag{4}
\]

The coulombic efficiency (\( \varepsilon_c \), also referred to as Faradic or current efficiency) was determined according to Equation (5) and corrected for leakage current:

\[
\varepsilon_c = \left| \frac{\int \text{charge} \cdot dt}{\int \text{charge} \cdot dt} \right| \cdot 100\% \tag{5}
\]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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