Electrochemical capacitors (ECs), also known as Supercapacitors or Ultracapacitors, have been developed for an assortment of energy storage applications. They are made of two porous conductive electrodes immersed in an electrolyte. Their main operating principle is based on the electrostatic attraction of ionic charges by oppositely-polarized solid electrodes in an electric double-layer region formed at electrode/electrolyte interfaces. Consequently, the energy stored in an EC is intrinsically physical. In an ideal electric double layer capacitor, the charge stored is proportional to the potential difference between the two electrodes (cell voltage). The maximum stable operating voltage of an EC is limited by thermodynamic stability of the electrolyte in the presence of the electrode material. When voltage exceeds a critical value the electrolyte tends to decompose, often with electrode surface corrosion that usually generates gas, which negatively impacts cell performance including its calendar life and cycle life. Although ECs are characterized by relatively low energy density, this energy is quickly available, which makes this technology most suitable for storing and delivering high-power pulses. ECs are commonly used to capture and store the regenerative braking energy of city transit buses, thereby reducing environmental pollution created by the burning of fossil fuels.

EC research intensity has increased tremendously in recent years with the development of new storage materials and the optimization of existing storage materials. Electrochemical capacitor performance measurements generally include capacitance, series resistance, leakage current, and open-circuit voltage decay. A guideline for reporting electrochemical capacitor performance metrics has recently been published. Although all such measurements provide important information, they do not express the dynamic performance of an active material, which is especially important when tasked with creating a minimum-size storage system for a specific power profile and thus quantify the storage system value. Other reported information often includes Ragone plots, which have only minor engineering importance—these plots are better used to compare different energy storage technologies than to design a storage system. A similar statement can be made for discharge-rate plots. Consequently, the functional value of the active material used in an electrochemical capacitor is not quantified via standard testing approaches.

In this study, dynamic performance information from a small prototype capacitor is scaled to a full-size energy storage system. The approach used is general and allows accurate scaling to most any size. The first step involves deriving an initial circuit model to represent the two-terminal electrical response of the prototype capacitor containing the active material. The second step involves modifying the initial model as necessary to increase its dynamic prediction accuracy. The third step involves designing the full-size storage system so that it precisely meets the power profile of a specific application. This design permits value quantification of the active material.

To develop an accurate equivalent circuit model for an electrochemical capacitor, it is necessary to understand that its electrical behavior is usually dominated by porous electrode processes due to the use of high-surface-area active material, most generally activated carbon. Publications from the 1960’s by de Levie discussed the influence of high-surface-area electrodes on device electrical performance and presented various transmission-line equivalent circuit models with distributed resistance and distributed capacitance. This was used by Garcia et al. in 2002 to estimate the dynamics of electrochemical reactions on planar electrode and by Lasia in 1995 to describe current distributions within an electrode. Song et al. investigated pore size distribution effects using impedance spectroscopy. Miller in 1995 used a truncated ladder network rather than a transmission line to represent the two-terminal electrical behavior of an EC. In 2004, Dougal et al. described an approach for determining the best ladder-network model, i.e. the optimum number of time-constants. Constant-phase-element models are often used to describe EC impedance behavior but they seldom are used to engineer an EC storage system. Pean et al. used molecular dynamics to create a transmission line model and predict EC behavior. An attempt to find the best model for low-power energy-harvesting systems was described by Weddell et al. Models for capacitor discharge curves, including temperature effects, have also been created. EC temperature effects alone are modeled by Gualous et al. Mahon et al. showed impedance data well-fitted to a model but with poor galvanostatic predictions. Models of several large commercial electrochemical capacitors were recently reported by Miller.

In this paper, we develop an equivalent circuit model for a prototype electrochemical capacitor and use SPICE (Simulation Program with Integrated Circuit Emphasis) circuit analysis software to validate the model. Once validated, the model is scaled in size to precisely meet power profile requirements of a specific application. Storage system performance is used to quantify active material value for that application. This approach uses value assessment of newly discovered active materials before commercial-size capacitors with these new ingredients become available.

Experimental

Electrodes preparation and prototype capacitor assembly.—EC electrodes were prepared from a mixture of activated carbon (Kuraray YP-50F) and dry PTFE binder (3% by mass). The ingredients
were mixed dry using a mortar and pestle to fibrillate the PTFE. Mixing continued until an intact homogeneous “dough” was formed, which was then rolled to a thickness of 200 μm using a calendering machine. Self-standing, 14-mm-diameter electrodes (each 13.4 mg) were punched and soaked in 1 mol L⁻¹ Li₂SO₄ aqueous electrolyte. Two wet electrodes were positioned facing each other on opposite sides of a 25-micrometer-thick polyolefin separator (Celgard) to create the prototype capacitor. This capacitor was sealed in a foil-pack with its two current-collector leads extending through the perimeter seal (Figure 1). Finally, the sealed capacitor was compressed between two steel plates using a screw-clamp. This prototype capacitor did not exhibit a high-frequency semi-circle in its complex-plane impedance plot, which is often the case with crimped-button-cell packaging.

Prototype capacitor measurements.—The two leads of the prototype capacitor were attached to a potentiostat/galvanostat (Bio-logic, France) using a true four-lead connection. Electrical measurements were performed using three voltage windows: 0.8 to 0.4 V, 1.2 to 0.6 V, and 1.6 to 0.8 V. The sequence began with 30 galvanostatic charge/discharge cycles at 0.4 A g⁻¹ to condition the capacitor. This was followed by electrochemical impedance measurements (EIS, 8 points per decade at a bias voltage of 0.75 times the upper voltage value, over the frequency range 1 mHz to 1 kHz) and then galvanostatic charge/discharge cycles at 0.16, 0.4, 0.8, 1.6, and 4.0 A g⁻¹. Final measurements were constant-power charge/discharge cycles over each voltage window at 0.16, 0.4, 0.8, 1.6, and 4.0 kW kg⁻¹.

Prototype modelling.—The impedance circuit-model fitting tool embedded in the EIS software was used to derive initial two- and three-time-constant equivalent circuit models for the three voltage windows. SPICE circuit simulation software “MicroCap” was then used to predict model performance. Comparisons were then made with constant-current charge/discharge measurements. Finally, circuit parameters were adjusted in an iterative fashion to improve model accuracy. This continued until no further model improvements could be realized. The circuit models were devised to accurately represent the two-terminal electrical response of the test cell - circuit elements in the models do not in any way represent actual physical processes that are occurring within the cell.

Results and Discussion

Prototype capacitor modelling.—Initial circuit model element values were derived using impedance data for each voltage window. Then, circuit element values were adjusted to improve the fit between model predictions and constant-current discharge data, including the voltage bounce-back region after the capacitor had been open-circuited upon reaching its minimum discharge voltage. Circuit element values for the two-time-constant optimized prototype capacitor model are listed in Table I. With this model, ~20% of the stored energy is available with a response time of R1 • C1 = 31 ms and 80% is available with a response time of (R1 + R2) • C2 = 0.5 s. Circuit element values for the three-time-constant optimized prototype capacitor model are listed in Table II. With this model, ~12%, ~81% and ~7% of the stored energy is available with respective response times of R1 • C1 = 19 ms, (R1 + R2) • C2 = 0.5 s, and (R1 + R2 + R3) • C3 = 1.4 s. Total capacitance for both models is the same (0.61 F).

Figure 2 compares constant-current discharge data (at 1.6 A g⁻¹) of both circuit models with simulation predictions. Discharge time (~12 s) is accurately predicted by both models (Figures 2a, 2b). Similarly, the initial IR “ohmic” drop is modelled with good accuracy by both the two- (Figure 2c) and the three-time-constant models (Figure 2d). Although discharge time and the initial voltage drop were modelled accurately, the rebound after open circuit (voltage bounce-back) was poorly predicted by the two-time-model constant (Figure 2e) while the three-time-model predicted this quite accurately (Figure 2f). The three-time-constant circuit model clearly was superior in predicting 1.6 A g⁻¹ constant-current discharge behavior of the prototype capacitor.

Predictions made using the optimized three-time-constant model were then compared with 10-mW constant-power discharge measurements, as shown in Figure 3 for voltage windows of 0.8 to 0.4 V, 1.2 to 0.6 V and 1.6 to 0.8 V. Figure insets have expanded time-scales to facilitate the comparisons at short-times. For 0.8 to 0.4 V operating window, model predictions accurately track constant-power discharge data at all times (Figure 3a). Minor differences are observed for a 1.2 to 0.6 V operating window. And greater differences are observed for the 1.6 to 0.8 V operating window, which may originate from redox processes associated with electrolyte decomposition and/or corrosion of the positive current collector, known to occur at voltage above ~1.5 V in aqueous lithium sulfate electrolyte.

Of course an equivalent circuit model is most useful when it predicts performance over a broad range of discharge rates and operating voltage windows. Figures 4a and 4b plot differences between the discharge time and model predictions respectively for constant-current and constant-power discharges, having durations of ~2 to ~100 s. Predicted constant-current discharge times are accurate to 3% for all three voltage windows. Predicted constant-power discharge times are accurate to 6% for all three voltage windows. Prior to using the model to design a storage system, it would be prudent to confirm its accuracy using replicate prototype capacitors.

| Table I. Element values of the optimized two-time-constant equivalent circuit model for the prototype capacitor. |
|-----------------|-------|-------|-------|
| R1 (Ω)          | 0.26  | 0.8   | 0.12  |
| R2 (Ω)          | 1     | 0.5   | 0.49  |
| R3 (Ω)          | 0.074 | 0.495 | 0.04  |
| C1 (F)          |       |       |       |
| C2 (F)          |       |       |       |
| C3 (F)          |       |       |       |

| Table II. Element values of the optimized three-time-constant equivalent circuit model for the prototype capacitor. |
|-----------------|-------|-------|-------|
| R1 (Ω)          | 0.26  | 0.7   | 30    |
| R2 (Ω)          |       |       |       |
| R3 (Ω)          | 0.074 | 0.495 | 0.04  |
| C1 (F)          |       |       |       |
| C2 (F)          |       |       |       |
| C3 (F)          |       |       |       |
Figure 2. Discharge data from 0.8 V to 0.4 V (a,b) with expansion showing initial ohmic drop (c,d) and open circuit voltage rebound (e,f) compared with model simulations: a,c,e) two-time-constant model, b,d,f) three-time-constant model. Dashed lines are experimental data and solid lines are model simulations.

Figure 5 compares measured and simulated Ragone plots (using the Table II three-time-constant model parameters). As shown for the 0.8 to 0.4 V operating window (Figure 5a), model predictions and measurements are identical. And for the 1.2 to 0.6 V operating window (Figure 5b), predictions and measurements are nearly identical. Differences become more apparent at low power levels for the 1.6 to 0.8 V operating window (Figure 5c), which again is probably related to the aforementioned irreversible reactions occurring at voltage above ∼1.5 V. These comparisons show that the upper operating voltage limit of the prototype capacitor is between 1.2 and 1.6 V, at least for discharge times lasting from 2 to 100 seconds. Our findings are in agreement with self-discharge results reported by Garcia-Cruz et al.,19 where changes from diffusion to activation control were noted above ∼1.4 V. Models with additional time-constants may be needed when using lower conductivity electrolytes (for instance, non-aqueous electrolytes) to achieve the level of accuracy herein reported.

Prototype scaling.—The concept of combining an internal combustion engine with an electric motor for hybrid propulsion creates the possibility of converting kinetic energy to potential energy during stopping, so-called regenerative braking energy storage. Kine-ematic calculations for stopping a vehicle travelling on a level road are straight-forward if the vehicle is treated as a point mass and energy losses are ignored. Then, vehicle kinetic energy is:

\[ E(t) = \frac{1}{2} M (V_0 - a_b t)^2 \]  

where M is the mass of the vehicle, \( V_0 \) its velocity when braking is first applied, \( a_b \) is braking deceleration, and t is braking time. Braking deceleration is assumed to be constant in this analysis.

The first derivative of \( E(t) \) with time yields braking power:

\[ P_b(t) = \frac{dE(t)}{dt} = -a_b M (V_0 - a_b t) \]  

Note that braking power is proportional to vehicle mass. Braking power \( P_b \) (defined to have a negative value) is at its maximum when braking starts then declines over time in a linear fashion during vehicle deceleration, reaching zero when vehicle motion stops. Thus, maximum braking power is \( P_{b(max)} = P_b(t = 0) = -a_b M V_0 \). Solving Eq. 2 for deceleration and inserting \( P_{b(max)} \) yields \( a_b = -P_{b(max)}/(M V_0) \). Braking time \( t_b \) is found by noting that \( P_b(t_b) = 0 \) and inserting \( a_b \).
Figure 3. Constant-power discharge simulations of the three-time-constant model compared with discharge measurements (10 mW) for three operating voltage windows: a) 0.8 to 0.4 V, b) 1.2 to 0.6 V, and c) 1.6 to 0.8 V. Dashed lines are experimental measurements and solid lines are three-time-constant model predictions. As shown, model accuracy is excellent at all times for the lowest-voltage window. (Figure insets have an expanded time scale to enhance comparisons at short times.)

Figure 4. Model prediction error maps for three operating voltage windows: a) constant-current discharge, b) constant-power discharge. Voltage window upper value: □ 0.8 V, ◦ 1.2 V, Δ 1.6 V. Lines are included to aid the eye.

Figure 5. Comparison of measured and simulated Ragone plots for three voltage windows: a) 0.8 to 0.4 V, b) 1.2 to 0.6 V, and c) 1.6 to 0.8 V. The dashed lines are experimental data while the solid lines are SPICE simulations of the three-time-constant equivalent circuit model (Table II element values).
Simulated prototype capacitor voltage during a five-second stopping event for a 0.6 to 1.2 V operating window with maximum braking power of −0.1415 W. The upper voltage level is reached in ∼4.4 seconds then slightly drops due to charge redistribution during the ensuing decline in braking power.

Figure 8. Simulated cumulative energy losses in the minimum-size bus capacitor storage system during stopping. The majority of the energy is lost in the first two seconds of braking when braking power is highest.

The braking time is:

\[ t_b = \frac{MV_o^2}{(-P_{\text{max}})} \tag{3} \]

Consider an example where \( M = 20,000 \text{ kg}, V_o = 20 \text{ km/hr} (5.56 \text{ m/s}) \), and vehicle stopping time is \( t_b = 5 \text{ seconds} \), values typical for one type of city transit bus. Bus kinetic energy at the time stopping begins is calculated using Eq. 1:

\[ E = \frac{1}{2} \cdot M \cdot V_o^2 = 309 \text{ kJ}. \]

Maximum braking power for this vehicle, calculated using Eq. 3, is:

\[ P_{\text{max}} = -\frac{20000 \cdot 5.56^2}{5} = -124 \text{ kW}. \]

Figure 6 shows the power profile for this application example.

Continuing with this example, a full-size transit bus energy storage system can be designed using the active material in the prototype capacitor. First note that the three-time-constant equivalent circuit model for the prototype capacitor (Table II parameters) was shown to accurately represent active material electrical performance for charge/discharge times of 5 seconds using a 0.6 to 1.2 V operating window. Scaling the prototype capacitor to the size needed for the transit bus is straightforward. First, \( n_1 \) prototype cells must be connected in series to meet the maximum voltage of the bus system, which we assume has a 300 to 600 V operating window. Then, for 1.2-V-rated prototype cells, \( n_1 = 600/1.2 = 500 \) cells. Maximum braking power in this example was −124 kW. Thus, braking power applied to each of the 500 series-connected cells in the bus system would be −124 kW/500 = −248 W. As shown in Figure 6, braking power applied to one of these series-connected cells would linearly ramp from −248 W to zero in 5 seconds during a stopping event.

SPICE circuit analysis software is used to determine the number of parallel-connected prototype capacitors needed to provide peak braking power of −248 W. Simulations show five-second charging of the prototype capacitor (from 0.6 to 1.2 V) with peak braking power of −0.1415 W (Figure 7). Thus, the cell needed for the transit bus would have a size equivalent to −248 W/−0.1415 W = 1753 prototype cells connected in parallel. A full-size cell for this transit bus application would have a capacitance value of 1753 • 0.61 F = 1069 F, which is the approximate size of a standard industrial product (1100 F). Then the transit bus energy storage system would be comprised of 500 cells in series, each cell having a rating of ∼1100 F. Size scaling from the prototype would be 1753 • 500 = 877,000 times. This represents almost six orders-of-magnitude size scaling. With this scaling approach, design accuracy should be no different than equivalent circuit model accuracy (<6% error).

These results show that active material mass in capacitors of the minimum-sized city transit bus storage system would be 877,000 cells • 2 electrodes/cell • 0.0134 g/electrode = 23.5 kg. Further, separator area in this minimum-sized capacitor storage system would be 1.54 cm²/cell • 877,000 cells = 135 m². Finally, with the assumption that active material makes up 25% of the capacitor’s mass, the estimated minimum-size capacitor storage system would have a mass of 100 kg, which represents an increase in bus mass of only ∼0.5%. Of course larger storage systems with greater mass and correspondingly higher costs could also be used. All reported scale-up values are minimum estimates and do not include, for instance, excess separator that is not located between capacitor electrodes. Actual values will intimately depend on details according to the cell design.

Storage efficiency during a five-second braking event can readily be determined for the full-size transit bus capacitor energy storage system. Total energy delivered to the storage system during bus stopping would be the kinetic energy of the bus, calculated at 309 kJ = 0.086 kWh. Storage system losses during a stopping event can be derived by integrating \( i^2R \) losses in circuit model simulations of the prototype capacitor. These results (Figure 8) show total losses reaching 29.1 kWh. The remaining kinetic energy (309 kJ − 29.1 kJ = 281 kJ) is stored in the capacitor system.

Based on circuit model simulations of a single stopping event, the capacitor system stored 281 kWh/309 kJ = 91% of the vehicle’s kinetic energy. The remaining 9% of the kinetic energy is dissipated in the capacitor since all other losses, for example rolling friction and air resistance, were ignored. These other losses would further reduce kinetic energy storage efficiency during a stopping event. Irrespective, stored regenerative braking energy does improve vehicle operating efficiency and thus reduce fuel consumption and greenhouse gas emissions.

**Active material “assessment value”**—The capacitor system in this transit bus example stored 281 kWh = 0.078 kWh of energy during
one stopping event. Assuming that energy costs 0.10 USD per kWh, then a single stopping event potentially saves energy with a value of 0.10 USD/kWh • 0.0078 kWh = 0.0078 USD. Admittedly this number is very small, but city transit buses typically operate for extended times each day and during most days of the week, which greatly increases this number. For concreteness, assume the transit bus makes 1000 stops each day and operates 330 days each year. Then using these assumptions, bus stopping energy would provide savings of 1000 • 330 • 0.0078 = 2,574 USD annually if the stored energy is effectively used for bus operation. The storage system in this example offers good potential for substantial savings because capacitors generally operate for many years. Noting that a full-size capacitor in the bus example had 23.5 kg of active material and yielded an annual savings of 2,574 USD, an arbitrary “assessment value” of 2,574 USD / 23.5 kg = 110 USD/kg can be assigned to the active material. This 110 USD/kg active material assessment value, of course, is valid only when the active material is used exactly like it was in the prototype capacitor (with the same formulation, i.e. binder, conductivity enhancer, etc.). Power profiles associated with other applications or capacitors having different designs would have completely different assessment values. The assessment value itself is not an important quantity but rather how it compares with values of other active materials that may be considered for use in the same application.

Conclusions

Equivalent circuit models were derived for a prototype electrochemical capacitor. Model prediction accuracy was examined over a wide dynamic range using constant-current and constant-power discharges and found to be accurate to within 6%. A circuit model of the prototype capacitor was scaled in size to create a storage system capable of capturing the regenerative braking energy from a full-size, 20-ton, city transit bus. Electrode mass, separator area, and energy storage efficiency were derived for this full-size storage system using circuit model simulations. An assessment value was assigned to the active material in the prototype capacitor, which was the ratio of annual energy cost savings to active material mass, for this specific application. This value is arbitrary but useful for comparing with other active materials used for the same application.

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