Supporting Information

Effective Electrochemical Charge Storage in the High-Lithium Compound \( \text{Li}_8\text{ZrO}_6 \)

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Experimental Section

Materials. Lithium benzoate (99%), zirconyl chloride octahydrate (>99%), zirconyl nitrate (99%), N-methyl-2-pyrrolidone (anhydrous, 99.5%), and Li foil (99.9%) were purchased from Sigma-Aldrich; polyvinylidene fluoride (PVDF) binder (>99.5%), Super P® conductive carbon black (>96%), battery electrolyte (1M LiPF₆ in 1:1:1 by volume ethylene carbonate:dimethyl carbonate:diethyl carbonate), 2032 coin cell cases and stainless steel spacers from MTI Corporation; Celgard 3501 membrane (monolayer polypropylene, 25 µm thick) from Celgard. Deionized water was purified to a resistivity higher than 18 MΩ·cm. All gases were purchased from Airgas. All chemicals were used without further purification.

Synthesis of nanosized Li₈ZrO₆/C. Zirconyl chloride octahydrate (1.5 mmol) and lithium benzoate (18 mmol) were mixed using a zirconia ball-and-cup set in a 8000M Mixer/Mill high-energy ball mill (SPEX SamplePrep) for 10 min to form a mixture containing a 12:1 molar ratio of Li:Zr. The mixture was pyrolyzed under N₂ (0.6 L/min) in a tube furnace with a ramp rate of 1 °C/min to 600 °C, followed by 2 h dwell time, and then with a ramp rate of 2 °C/min to 800 °C, followed by 2 h dwell time. The sample was cooled under N₂ to room temperature before being removed from the tube furnace. The sample was ball milled for a total of 30–60 min in 10 min intervals using an alumina ball-and-cup set in a ball mill. An XRD pattern was obtained after each 10 min interval and ball milling was stopped when impurity peaks were first observed at d-values of 0.478 nm (Li₆Zr₂O₇) or at 0.287 and 0.292 nm (Li₂CO₃). The final products were found to contain 20–30 wt% carbon, as determined using the combustion-based analysis at Atlantic Microlabs, Norcross, GA. The variation in carbon content is believed to arise from small differences in the ball milling treatment, where differential loss/segregation of carbon and Li₈ZrO₆ phases may occur, as well as to small differences in the pyrolysis process when different tube furnaces were employed. These samples are referred to as Li₈ZrO₆/C.

Synthesis of nanosized Li₆Zr₂O₇/C. Zirconyl nitrate (2 mmol) and twice the equivalent mass of Super P carbon were ball-milled in a hardened zirconia ball-and-cup set (SPEX SamplePrep) for 10 min. The nitrate/carbon composite was calcined under static air by ramping from room temperature to 400 °C at a ramp rate of 2 °C/min with no hold and then cooled naturally back to room temperature. After the ZrO₂ content of this material was determined by thermogravimetric analysis, the ZrO₂/C composite was ball-milled with an appropriate amount of lithium benzoate (3.6 mol:mol Li:Zr) and pyrolyzed under N₂ (0.5 L/min) with a 1 °C/min ramp rate to 600 °C,
followed by holding for 2 h, then 2 °C/min to 800 °C, followed by holding another 2 h. The sample was allowed to cool completely to room temperature before being removed from the inert atmosphere.

*Battery assembly.* To prepare the active material for a battery electrode, the Li$_8$ZrO$_6$/C and Super P conductive carbon black (Super P) were ball milled for 5 min into fine powder using an alumina ball-and-cup set in a ball mill. A 5 wt % dispersion of polyvinylidene fluoride in NMP was added to achieve a final composition of 70:20:10 by mass of Li$_8$ZrO$_6$/C:SuperP:PVDF. Alternatively, electrodes were also prepared using 90:10 by mass of Li$_8$ZrO$_6$/C:PVDF with no added Super P carbon. The mixture was ground further using a mortar and pestle to obtain a heterogeneous slurry. The mixture was cast onto a carbon-coated aluminum foil into a thin film with a thickness of less than 200 µm using a doctor blade. The film was prepared and dried at ambient temperature in a dry room with less than 100 ppm of H$_2$O or less than 1% relative humidity during active use. The film was transferred to a vacuum oven kept at 110 °C overnight to remove excess NMP. The dried film was pressed using a mechanical roller to a final thickness of ~40 to 50 µm and the electrodes (9/16 inch in diameter) were punched out. The loading of active material in the electrodes was typically between 1 and 1.5 mg (0.6–1 mg/cm$^2$). The electrodes were assembled into CR2032 coin cells in a half-cell configuration using metallic lithium as the counter electrode, a Celgard 3501 membrane as the separator, and ~0.25 g of 1 M LiPF$_6$ in EC:DMC:DEC as the electrolyte. The coin cells were pressed using a coin cell crimper with a pressure of at least 150 psi for 15 s. All the cell assembly was performed in a He filled glove box. After addition of the electrolyte, the cells were allowed to rest for at least 10 h to ensure complete infiltration of the electrode with the electrolyte solution. The coin cell assembly is shown in Fig. S1.
**Figure S1.** Diagram illustrating the assembly of the coin cells used in this study. The photographs show the electrode film from which a circular electrode had been punched out and a fully assembled CR2032 coin cell. LZO composite refers to Li$_8$ZrO$_6$/C

**Characterization of materials.** Powder X-ray diffraction patterns of the samples were obtained with an X’Pert Pro diffractometer (PANAnalytical) with an X’Celerator detector. The radiation source was a Co anode with $\lambda = 1.789$ Å. Samples were ground into a fine powder, then placed on a flat bracket sample holder. The scans were collected at 45 kV and 40 mA.

Scanning electron microscopy (SEM) images were taken using a JEOL 6700 SEM at 5 kV accelerating voltage and 10 mA current. The samples were coated with platinum with a thickness of 50 Å to increase their conductivity for SEM imaging.

For transmission electron microscopy (TEM) of Li$_8$ZrO$_6$, 200 mg of Li$_8$ZrO$_6$ was dispersed in 10 mL of various solvents. The mixtures were bath sonicated for 1 h and then centrifuged at 500 rpm for 5 minutes. The top aliquot of the mixture was drop-cast onto formvar-coated Cu grids. The samples were dried in a vacuum oven at 50 °C for 2 h. TEM images were obtained using a Tecnai T12 microscope operated at 80 kV with a LaB$_6$ filament.

Electrochemical tests were performed using an Arbin battery-testing system BT2000 workstation. The coin cells were left at rest for 10 h for better infiltration of electrolyte into the active material on an electrode. The Galvanostatic charge-discharge measurements were performed at various charge/discharge rates (C rate, with $C$ defined as 110.5 mA/g Li$_8$ZrO$_6$) with the current calculated from the mass of the active material in an electrode in the potential range from 1.3 to 4.5 V (sometimes to 4.7 V). Capacity restriction limits were set at 110.5 mAh/g, 221 mAh/g, or
331 mAh/g Li$_8$ZrO$_6$, and the battery tester was set to switch between the charge and discharge processes when either the potential limit (1.3 and 4.5 or 4.7 V) or the capacity limit condition was fulfilled. Specific conditions are described in the figure captions throughout the text. Cyclic voltammograms of coin half-cells were collected on a CHI660C potentiostat (CH Instruments, Austin, TX), using scan rates between 0.05 and 0.8 mV/s.

For galvanostatic intermittent titration technique (GITT) studies, electrochemical tests were performed using an Arbin battery-testing system BT2000 work station. Coin cells containing 90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF were left at rest for 10 h for better infiltration of electrolyte into the active material of the electrode. A current of 10.5 mA (corresponding to a current rate of C/2) was applied to the coin cell for 1 min, then the coin cell was relaxed for 10 h. The equilibrium potential was determined at the end of the 10-h relaxation periods. The pulse–relaxation process was repeated until either 0.5 or 3 Li/formula unit were removed from the active material Li$_8$ZrO$_6$ to reach a value of $x = 7.5$ or 5 in Li$_x$ZrO$_6$, respectively. The data from each pulse were used to plot V vs. $\sqrt{t}$ for the calculation of the diffusion coefficient.

Electrochemical impedance spectroscopy (EIS) measurements were carried out on a Solartron SI1287 electrochemical interface coupled with a Solartron SI1255B frequency response analyzer. The impedance spectra were collected using a sinusoidal perturbation with an amplitude of 10 mV and a sweep rate of 10 scans per decade within the frequency range of 0.01 Hz to 1 MHz. The impedance spectra were fitted using the Z-Fit function of the EC-lab impedance fitting tool.

The conductivity of the Li$_8$ZrO$_6$ and Li$_8$ZrO$_6$/C composite materials was measured by chronoamperometry. For this purpose, bulk Li$_8$ZrO$_6$ and Li$_8$ZrO$_6$/C composite samples were ball-milled for 10 min into fine powders. For bulk Li$_8$ZrO$_6$, 200 mg of material was pressed into pellets with a diameter of 13 mm using a hydraulic press at a ram pressure of 8 tons for 10 min. The typical thickness of a bulk Li$_8$ZrO$_6$ pellet was ~0.7-0.8 mm. For Li$_8$ZrO$_6$/C composites, 250 mg of material was pressed into pellets with a diameter of 13 mm using a hydraulic press at a ram pressure of 8 tons for 30 min. The typical thickness of a Li$_8$ZrO$_6$/C composite pellet was ~0.6-0.7 mm. Both sides of the pellet were coated with silver paste, using a wooden applicator. Chronoamperometry measurements were conducted with a potential of 0.1 V over a period of 1000 seconds using a CHI 600C potentiostat. In this technique, the potential of the cell is stepped and the resulting current decay is monitored and fitted to extract electronic and ionic conductivity values.
X-ray photoelectron spectroscopy was performed using a Surface Science SSX-100 instrument. The XPS peak positions were calibrated against the C\textsubscript{1s} peak at 284.6 eV.

The electrolyte stability during cycling was studied by NMR. 1 M LiPF\textsubscript{6} in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1/1/1 volume ratio) from MTI corporation was used as the electrolyte. The electrolyte was used in 15 coin cells during the battery testing using the following program: charging at C/5, discharging at C/10 between 1.3 and 4.5 V with a capacity restriction of 110.5 mAh/g for 5 cycles; this was followed by charging at C/5 and discharging at C/10 for 10 cycles in the 1.3–4.5 V voltage range with a capacity restriction of 221 mAh/g. After the battery testing, the 15 coin cells were opened in a He-filled glove box using pliers. A syringe was used to withdraw the electrolyte between the cathode and the membrane of the coin cells. The battery electrolyte sample was filtered using a 0.20 μm polytetrafluoroethylene (PTFE) membrane before mixing with the NMR solvent, deuterated dimethyl sulfoxide (DMSO-d\textsubscript{6}). A control sample was made by mixing fresh electrolyte with DMSO-d\textsubscript{6}. Samples for proton (\textsuperscript{1}H) and fluorine (\textsuperscript{19}F) NMR were prepared under a helium atmosphere in a glove box. Prior to use, DMSO-d\textsubscript{6} was dried over freshly activated 3A molecular sieves. Samples were dissolved in dried DMSO-d\textsubscript{6} and sealed in an NMR tube with paraffin wax film (Parafilm M). \textsuperscript{1}H and \textsuperscript{19}F NMR spectra were collected using a Bruker Avance III HD with a SampleXpress attachment (AX-400).

\textit{Ex-situ X-ray diffraction.} Ex-situ X-ray diffraction patterns of electrodes at different states of charge were obtained with an X'Pert Pro diffractometer (PANAnalytical) with an X'Celerator detector. The radiation source was a Co anode with λ = 1.789 Å. A separate cell was used for each experiment, prepared from the same batch of electrode material for each cell. After each experiment, the coin cell was opened and the electrode was quickly washed with excess dimethyl carbonate and dried by blowing house nitrogen gas over it for 30 s. The electrode was taped on the XRD sample holder with carbon tape to achieve a flat surface. A fast (30 min) survey XRD scan was obtained before and after the longer 12-h scans shown in this figure to detect any changes due to exposure of the sample to air. The Al peaks originate from the current collector and were used as an approximate internal standard for intensities. A Li\textsubscript{2}CO\textsubscript{3} phase was observed for two cells (1 Li – charge and 1 Li – full cycle), but was much less pronounced in the other cells. This phase formed during exposure of the electrode to air in this ex-situ experiment and was never observed in \textit{operando} experiments.

\textit{Operando synchrotron X-ray diffraction.} \textit{Operando} synchrotron X-ray diffraction studies were
carried out at beamline 17BM-B ($\lambda = 0.45260(2)$ Å, detector distance 500 mm) at the Advanced Photon Source, Argonne National Laboratory, using AMPIX cells. Electrodes, 13 mm in diameter and between 23.3 and 25.9 mg in total mass, were prepared in an Ar-filled glovebox, using a mixture of 80 wt% Li$_8$ZrO$_6$/C (24.9 wt% C, 1.07 wt% N, 0.65 wt% H, 12 wt% Li$_2$O) and 20 wt% PTFE binder. No additional carbon was added. The AMPIX half-cells were assembled using these cathodes with Li foil (380 µm thick, 9/16” diameter) and a glass microfiber separator (5/8” diameter). The electrolyte was 1 M LiPF$_6$ in a 1:1:1 (by volume) mixture of EC/DMC/DEC. Cells were cycled galvanostatically in the beamline using a Maccor 4300 battery cycler. A LaB$_6$ standard was used as reference to determine instrumental peak broadening and to create the image controls used for integration of 2D diffraction images. An AMPIX cell containing only Li foil, electrolyte solution, and the glass fiber separator was used to correct for the background signal. These experiments were carried out at room temperature. Data were analyzed using the GSAS-II program. Peak fitting was carried out using Origin software. Alternatively, peak areas were determined by fitting six Lorentzian curves to the diffraction patterns. The background was removed prior to curve fitting by fitting a 7-degree Chebyshev series using to the background and subtracting it from the pattern. The Lorentzian curves were fit using the Python SciPy package and the background was fit using the Python NumPy package.

Synchrotron X-ray structure analysis by pair distribution function (PDF) analysis. PDF analysis was carried out at beamline 11-ID-B at Argonne National Laboratory to study the local structure of the Li$_8$ZrO$_6$ cathode at different states of charge, disordered reaction phases, and potential side products formed during electrochemical cycling. Multiple coin cells were charged and discharged to different states of charge. The coin cells were then opened in an Ar-filled glove box. The cathode materials were removed from the current collectors and sealed in capillary tubes for PDF analysis at room temperature. X-ray scattering data suitable for PDF analysis were collected at beamline 11-ID-B at the Advanced Photon Source at Argonne National Laboratory. High energy X-rays (wavelength 0.2114 Å, 58.6 keV) were used in combination with a large amorphous silicon-based area detector. Total scattering data were collected using a short sample-to-detector distance (~18 cm) to $Q_{max} = 23$ Å$^{-1}$. The X-ray scattering images were reduced within QXRD and FIT2D. Pair distribution functions (PDFs) were extracted from the total scattering data within PDFgetX2, correcting for background and Compton scattering. Data were collected for 3 min total exposure at a sample to detector distance of 18 "d18". Data suitable for powder
diffraction analysis/Rietveld refinement were collected at the longer sample to detector distance "d95". Structure models were fitted using PDFgui and cif files from the Crystallography Open Database (Li$_2$O: COD 1514086; Li$_6$Zr$_2$O$_7$: COD 1536206; Li$_2$ZrO$_3$: COD 1008200; Li$_2$CO$_3$: COD 9008283, monoclinic ZrO$_2$: COD 2300544; tetragonal ZrO$_2$: COD 1525705), the Materials Project (orthorhombic carbon: mp-568286) and crystallographic data for Li$_8$ZrO$_6$ from Huang et al.\textsuperscript{6}

**Computational Section**

*Density functional calculations.* Quantum mechanical calculations were carried out employing HSE06\textsuperscript{7} exchange-correlation density functionals as described by Huang et al.\textsuperscript{6} The PBE+U method was also used, in which the Coulomb and exchange interactions of the $p$ orbitals of O are corrected by setting the Hubbard parameter $U$ to 6 eV,\textsuperscript{8-10} and the other electrons are treated by the uncorrected PBE exchange-correlation functional. All calculations included spin polarization. Both the coordinates of the atoms and the lattice constants were optimized.

The averaged Li cell potentials vs. Li/Li$^+$ were calculated as:

$$V = -\frac{1}{F} \frac{E(Li_xZrO_6) - E(Li_{x-\Delta x}ZrO_6) - \Delta x E(Li)}{\Delta x}$$  \hspace{1cm} (1)

where $E$ is the total energy, and $F$ is the Faraday constant. These are average potentials over the range of $x$ from $x-\Delta x$ to $x$. 

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Supplementary Figures

*Morphology of delaminated Li$_8$ZrO$_6$ particles*

**Figure S2.** SEM (a) and TEM images (b, c) of Li$_8$ZrO$_6$ particles that had been partially delaminated by bath sonication for 1 h in various solvents (as indicated in the figure, 20 mg/mL) and recovered from the supernatant after centrifugation. The particle in the top left part of the SEM image in (a) is representative of the original particles. The other particles illustrate the 2D sheet structure of this pseudolamellar material. Samples for TEM were prepared by adding a drop of the centrifuged supernatant onto a TEM grid and drying the grid in a vacuum oven at 50 °C for 1.5 h. The XRD patterns in (d) demonstrate that the Li$_8$ZrO$_6$ structure is retained after dispersion in these solvents, resedimentation, and drying in a vacuum oven at 100 °C. (Note that these Li$_8$ZrO$_6$ samples were prepared by a bulk synthesis, using LiNO$_3$ and ZrO(NO$_3$)$_2$ as precursors.\textsuperscript{6,11}) We thank B. E. Wilson for assistance with the SEM image.

\textsuperscript{6} G. Liu et al., *J. Phys. Chem. C* **2016**, *120*(4), 2106–2113
\textsuperscript{11} G. Liu et al., *Bull. Chem. Soc. Jpn.* **2014**, *87*(6), 645–654
Figure S3. Scanning electron microscopy (SEM) backscattered electron image and energy-dispersive X-ray spectroscopy (EDS) Zr, C, and O maps of Li$_8$ZrO$_6$/C particles. These images were taken using a JEOL 6500 SEM at 5 kV accelerating voltage and 10 mA current. Samples were dispersed in THF (3.33 mg/mL) and sonicated for 15 minutes. The dispersion was drop-cast onto a silicon wafer, and then allowed to dry at room temperature. The samples were coated with platinum with a thickness of 50 Å to increase their conductivity for SEM imaging. We thank Thomas E. Webber for assistance with SEM-EDS.
Charge transport in Li$_8$ZrO$_6$ and Li$_8$ZrO$_6$/C composites

Figure S4. (a) Experimental set-up used for the chronoamperometry measurements. (b) Chronoamperometry trace for bulk Li$_8$ZrO$_6$ at room temperature.

Figure S5. GITT curve of a Li$_8$ZrO$_6$/C cathode as a function of time. The coin cell was charged with a constant current of 10.5 mA followed by an open circuit condition for 10 h to allow the coin cell potential to relax to its equilibrium condition. A representative GITT curve for a charging pulse and a relaxation period is shown in Fig. S7. The equilibrium potential was reached when the change of the coin cell potential over a one-hour range ($dE/dt$) was less than 10$^{-6}$. For all of the GITT curves, 10-h relaxation was sufficient for the coin cell to reach its equilibrium potential.
Figure S6. Equilibrium potential at different states of charge. The equilibrium potential between the charge and discharge processes showed a hysteresis loop, indicating the polarization of the electrode during the electrochemical testing.

Figure S7. A representative voltage vs. time plot for the charging pulse and the relaxation process. The inset is the expanded version, showing the first 60 seconds during which a current of 10.5 mA was applied to the coin cell (corresponding to the current rate of C/2) and the beginning of the relaxation process. The coin cell was relaxed for 10 hours after the charging pulse. The equilibrium potential was recorded at the end of the relaxation process.
Figure S8. The potential vs. $t^{1/2}$ was plotted for each GITT pulse. A representative $V$ vs. $\sqrt{t}$ plot is shown here. A straight-line fit was performed over the region 4–8 s$^{1/2}$ for the determination of $dE/dt^{1/2}$. The straight line fit of the potential profile indicates zero-order kinetics or the independence of potential on time. Fick’s second law of diffusion was applied to determine the chemical diffusion coefficient of Li ($D_{Li}$). The equation for $D_{Li}$ for sufficiently small current and small changes of potential over the electrode composition ($dE/dx$) can be written as:

$$D_{Li} = \frac{4}{\pi} \left( \frac{I_0 V_M}{S} \right)^2 \left[ \left( \frac{dE}{dx} \right) \left( \frac{dE}{d\sqrt{t}} \right) \right]^2$$

for $t \ll \frac{t^2}{D_{Li}}$ (2)

where $I_0$ is the current, $V_M$ the molar volume, $S$ is the contact area between electrolyte and sample, taken to be the cross-sectional area of the electrode, $l$ the thickness of the electrode, $z_i = 1$ for Li$^+$, and $F$ the Faraday constant. Values of $dE/dx$ were determined from the slopes in the equilibrium potential plot (Fig. S6).

Figure S9. Room temperature Li-ion diffusion coefficient (log scale) in Li$_x$ZrO$_6$ at different states of charge.
Figure S10. (a) Lattice constant values calculated by (a) HSE06 and (b) PBE+U, (c) volumes of the primitive unit cell and (d) average voltages for delithiation of Li$_x$ZrO$_6$, computed by HSE06 and PBE+U (see also Table S2).
Figure S11. (a) XRD pattern of the electrode in an AMPIX cell before any galvanostatic cycling. The background from a cell with all components except Li$_8$ZrO$_6$/C was subtracted from this pattern. Indexed peaks correspond to Li$_8$ZrO$_6$. The other peaks are assigned as indicated. The peak marked with an asterisk is at the position of the most intense peak for Li$_6$Zr$_2$O$_7$ and is assigned to this minor impurity phase. Several other, much weaker Li$_6$Zr$_2$O$_7$ peaks could be found in an expanded version of this plot. (b) Voltage vs. capacity curves for the AMPIX cell during galvanostatic cycling. The cell was charged and discharged galvanostatically for 7 cycles at C/3 with voltage limits between 1.3 and 4.7 V vs. Li/Li$^+$. After 7 cycles, the voltage limits were removed to allow a deeper charge.
Figure S12. (a) Intensity of the (111) peak of Li$_2$O and (b) the (22-3)/(402) Li$_8$Zr$_2$O$_7$ peak at $\sim$49.4° 2θ (Co Kα) as a function of the depth of charge during the 8 charge and discharge steps for the AMPIX cell. Li$_2$O peaks remained relatively constant in intensity until removal of 6 Li from Li$_8$ZrO$_6$, then they also decreased in intensity but did not disappear completely. The intensity of the (22-3)/(402) Li$_8$Zr$_2$O$_7$ peak at $\sim$49.4° 2θ (Co Kα) drops faster with cycling than the intensities of the Li$_8$ZrO$_6$ peaks. It drops as fast on discharging as on charging.
Galvanostatic cycling of Li$_8$ZrO$_6$/C electrodes

**Figure S13.** Charge and discharge capacities for Li$_8$ZrO$_6$/C half cells as a function of cycle number. Potentials were limited between 1.3 and 4.5 V vs. Li/Li$^+$. Charge capacities were restricted to the values shown (red, blue) or they remained unrestricted (black). A charge capacity restriction significantly improves the discharge capacity retention. The electrode for the data in red contained 90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF; for this cell the charge rate was C/5 and the discharge rate C/10. The electrodes for the data in black and blue contained 70 wt% Li$_8$ZrO$_6$/C, 20 wt% Super P carbon and 10 wt% PVDF, with a 52 wt% content of Li$_8$ZrO$_6$ in the electrode; for these two cells the charge and discharge rates were both C/5. The black and blue curves are the same as those shown in Fig. 4 of the main manuscript. For the red curves in Fig. 4 and S13, the electrode composition and the discharge rates are different. LZO refers to Li$_8$ZrO$_6$. 

LZO refers to Li$_8$ZrO$_6$. 

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Figure S14. (a) Charge and discharge capacities for a Li$_8$ZrO$_6$/C coin half-cell with an electrode composition of 90 wt% Li$_8$ZrO$_6$/C (~26–27 wt% of this is carbon) and 10 wt% PVDF. The cell was charged and discharged at room temperature for 12 cycles at C/5 with a capacity restriction of 221 mAh/g. Starting at cycle 13, it was charged at C/5 but discharged at C/10 and maintained ~100% Coulombic efficiency for at least 88 cycles. (The deviations from 100% during later cycles are related to equipment having to be moved due to scheduled power outages.) (b) Charge and discharge curves for selected cycles.
Figure S15. Selected charge and discharge curves for the coin half-cells for which data are shown in Fig. 5. (a)–(c) Charge and discharge curves for selected cycles corresponding to Fig. 5a,b. (a) As charge potentials increased steadily during the first nine cycles, the Coulombic efficiency reached 100% at cycle 9. (b) The charge voltage at high capacities continued to increase during cycles 10–30. The plateau seen during charging between ~110 and 221 mAh/g disappeared by cycle 30, resulting in a continuously sloping charge curve. By cycle 50, the discharge potential had reached a plateau at ~1.65 V vs. Li/Li\(^+\) between 110 and 221 mAh/g. (c) The charge potential between cycles 60 and 100 all remained below 4 V vs. Li/Li\(^+\). (Due to a power outage during discharge in cycle 54, the coin cell was disconnected from the original testing instrument (Arbin) and transferred to a different instrument in another building to complete the test. The entire moving process took place over approximately 3 h. This interruption allowed the coin cell to rest, which likely resulted in the decreased polarization.) A potential step was observed during charging near 110 mAh/g. The discharge potentials were relatively level (between 1.8 and 1.6 V vs. Li/Li\(^+\)) between 65 mAh/g and 221 mAh/g for many cycles, but the onset of this plateau and its small slope increased with cycle number. Out of the 180 total cycles, 130 cycles were observed in which Coulombic efficiency was close to 100% (cycle 8 to 137). All of these were within the voltage range of 1.3–4.7 V vs. Li/Li\(^+\). 66 of them were in the range 1.3–4.5 V, 46 in the range 1.5–4.5 V, and 30 continuous cycles in the range 1.5–4.0 V. (d)–(f) Charge and discharge curves for selected cycles corresponding to Fig. 5c,d. (d) The first five cycles were carried out with a capacity limit of 221 mAh/g to condition the cell. The cell reached 100% Coulombic efficiency on the 5th cycle. (e) After the capacity limit was raised, it took five more cycles to reach 100% Coulombic efficiency again (Cycle 10). The charging potential decreased during these cycles and the discharge capacity and energy improved. (f) During cycles 12 to 22 the charging potential increased gradually. At cycle 20, it increased to a value that led to partial oxidation of the electrolyte, which led to a decrease in discharge capacity after cycle 27. During these cycles, the discharge potential below 200 mAh/g first increased then decreased with the number of cycles; between 200 and 331 mAh/g, however, the discharge potential stayed flat and relatively constant each cycle.
Figure S16. Charge and discharge capacities and Coulombic efficiencies for a Li$_8$ZrO$_6$/C coin half-cell with an electrode composition of 90 wt% Li$_8$ZrO$_6$/C (~26–27 wt% of this is carbon) and 10 wt% PVDF. The cell was conditioned for five cycles with a capacity restriction of 110.5 mAh/g. It was then galvanostatically charged at C/5 and discharged at C/10 at room temperature for 5 or 6 cycles each with progressively wider voltage windows and limits set in the ranges 1.5–4.0 V, 1.5–4.2 V, 1.5–4.5 V, and 1.3–4.5 V vs. Li/Li$^+$ and no capacity restrictions.

Figure S17. Rest potential vs. time for coin half-cells with a cathode composition of Li$_8$ZrO$_6$/C:PVDF = 90:10. The cell was conditioned for 5 cycles at C/5 charge and discharge rates and a capacity restriction of 110.5 mAh/g Li$_8$ZrO$_6$. It was then charged at C/5 and discharged at C/10 for 5 cycles with capacity restriction 221 mAh/g Li$_8$ZrO$_6$, charged for one additional step at C/5 to 221 mAh/g Li$_8$ZrO$_6$, and then left in this state.
Figure S18. (a) Specific capacities of a coin half-cell with a cathode containing 90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF. Specific capacities are shown with respect to Li$_8$ZrO$_6$. The cell was cycled with a current rate of C/5 on charging and C/15 on discharging at room temperature. The capacity limit was set to 221 mAh/g for the first 6 cycles using a C/5 charge rate and C/10 discharge rate. Starting at cycle 7, the capacity limit was raised to 331.5 mAh/g and the discharge rate lowered to C/15. At this discharge rate, the Coulombic efficiency remains 100% immediately after the increase in the charge limit. Voltage limits were set from 1.3 to 4.7 V. Selected charge and discharge curves for this cell are shown in (b) and (c). With the capacity limit set to 221 mAh/g, even though the first cycle showed abnormal behavior during charging, subsequent cycles follow normal cycle behavior, and 100% Coulombic efficiency was reached by cycle 4. In the early cycles at 331.5 mAh/g, the charging potential drops slightly and the discharging potential increases at high specific capacities (> 300 mAh/g), but in later cycles these trends are reversed. However, at lower specific capacities, the discharge potential increases monotonically throughout these cycles.
Analysis by Electrochemical Impedance Spectroscopy (EIS)

Figure S19. EIS spectra of a coin half-cell (90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF) charged at C/5 to remove 1 Li/f.u. and discharged at C/10 for 5 cycles each. The full range is shown on the left and an expanded region on the right.

Figure S20. EIS spectra of coin half-cells (90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF) at different states of charge as indicated in the figure. Charge rates of C/5 and discharge rates of C/10 were used.

Figure S21. Equivalent circuit used for modeling the electrochemical impedance spectroscopy data. $R$ is resistance, $Q$ is a constant phase element. $R_1$ is the electrolyte resistance. The combination of $R_2$ and $Q_2$ is related to a passivating layer on the electrode surface. The combination of $R_3$ and $Q_3$ is related to charge transfer. The last element $Q_4$ is related to diffusion and differential capacity.\textsuperscript{11}
**Ex-situ XRD measurements**

**Figure S22.** Charge/discharge curves for the cells described in Fig. 6. Charge rates of C/5 and discharge rates of C/10 were used. The following electrode masses (Li$_2$ZrO$_6$ masses) were used: (a) 1 Li – charge: 2.5 mg (1.6 mg); (b) 1 Li – full cycle: 2.8 mg (1.8 mg); (c) 2 Li – charge: 4.2 mg (2.7 mg); (d) 2 Li – full cycle: 3.4 mg (2.2 mg); (e) 3 Li – charge: 5.9 mg (3.8 mg); (f) 3 Li – full cycle: 5.8 mg (3.8 mg).
Figure S23. Relative peak intensities of characteristic Li$_8$ZrO$_6$ or Li$_6$Zr$_2$O$_7$ XRD peaks compared to peaks of the Al current collectors. The relative peak intensities are shown on the vertical axes and cell numbers correspond to the cells whose XRD patterns are shown in Fig. 6. Cell 0: before cycling; cell 1: 1 Li – charge; cell 2: 1 Li – full cycle; cell 3: 2 Li – charge; cell 4: 2 Li – full cycle; cell 5: 3 Li – charge; and cell 6: 3 Li – full cycle. The black and blue traces are intended to guide the eye. The XRD peaks were ratioed to Al$_{(111)}$ (black) and Al$_{(200)}$ (blue) peak intensities, respectively. Differences in relative peak intensity patterns between these graphs are due to partial overlap of the Li$_8$ZrO$_6$ (003) and (101) peaks with a carbon background and with an Li$_6$Zr$_2$O$_7$ peak and due to the low absolute intensities of some of these peaks.
Ex-situ synchrotron X-ray structure analysis by PDF analysis

Figure S24. Ex-situ PDF patterns of electrode films made from a Li$_8$ZrO$_6$/C composite with 90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF (purple), and of electrode films with the same composition after different states of charge. These electrodes contain ~58 wt% Li$_8$ZrO$_6$. A separate cell was used for each experiment, prepared from the same batch of electrode material for each cell. This material contained small amounts of Li$_6$Zr$_2$O$_7$ and Li$_2$O impurity phases. (a) Constant peaks related to carbon. (b) Constant peaks related to Li$_8$ZrO$_6$. (c) Peaks changing partially reversibly. (d) Peaks changing irreversibly.
Figure S25. PDF data (purple) for an electrode film made from a Li$_8$ZrO$_6$/C composite with a nominal composition of 90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF. The red curve is a fit for a composite consisting of 63% Li$_8$ZrO$_6$, 21% C, 5% Li$_2$O, 1% Li$_6$Zr$_2$O$_7$ and 10% PVDF. The difference curve is shown in green. Structure models were fitted using PDFgui and cif files from the Crystallography Open Database (Li$_2$O: COD 1514086; Li$_6$Zr$_2$O$_7$: COD 1536206), the Materials Project (orthorhombic carbon: mp-568286) and crystallographic data for Li$_8$ZrO$_6$ from Huang et al.\textsuperscript{6}
Figure S26. Simulations for different atom pairs in Li$_8$ZrO$_6$ (red curves) superimposed on the experimental PDF curve of the electrode film described in Figure S25. These simulations were used for assigning features in the overall PDF curve of the electrode film. Structure models were fitted using crystallographic data for Li$_8$ZrO$_6$ from Huang et al.$^6$
Figure S26 (continued). Simulations for different atom pairs in tetragonal and monoclinic ZrO$_2$, Li$_2$O, carbon, and Li$_6$Zr$_2$O$_7$ (red curves) superimposed on the experimental PDF curve of the electrode film described in Figure S25. Structure models were fitted using PDFgui and cif files from the Crystallography Open Database (Li$_2$O: COD 1514086; Li$_6$Zr$_2$O$_7$: COD 1536206; monoclinic ZrO$_2$: COD 2300544; tetragonal ZrO$_2$: COD 1525705), and the Materials Project (orthorhombic carbon: mp-568286).
Figure S26 (continued). The PVDF structure was approximated from the molecular structure of the monomer.
**Figure S27.** Interatomic Zr…O, Li…O, O…O, and Zr…Zr distances calculated using CrystalMaker 9.2 software using crystallographic information files (.cif) generated from HSE06 calculations for the lowest energy structures of Li$_x$ZrO$_6$, $x = 8, 7, 6, 5$. 
Figure S27 (continued). Interatomic Zr…O, Li…O, O…O, and Zr…Zr distances calculated using CrystalMaker 9.2 software using crystallographic information files (.cif) generated from HSE06 calculations for the lowest energy structures of Li$_x$ZrO$_6$, $x = 8, 7, 6, 5$. 

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Interatomic Distances (HSE06): O…O

Interatomic Distances (HSE06): Zr…Zr
Involvement of oxygen in redox processes

Figure S28. XPS survey spectra of as-made, bulk Li$_8$ZrO$_6$ (black), a Li$_8$ZrO$_6$/C composite electrode before charging (blue, labeled “Electrode film”: 70 wt% Li$_8$ZrO$_6$/C: 20 wt% Super P carbon: 10 wt% PVDF; 53 wt% Li$_8$ZrO$_6$ in the electrode) and electrodes that had been cycled five times at C/20 with a charge capacity limit of 110 mAh/g, and then charged at C/50 until either 1 Li/f.u. (green) or 3 Li/f.u. (red) had been removed, assuming that all charge was related to removal of Li.
Potential capacity contributions from other coin cell components

Several control experiments were carried out to determine whether the observed capacity can be mainly related to the Li$_8$ZrO$_6$ phase, or whether alternative sources contributed significantly to the capacity. In particular, we examined possible contributions from the Li$_6$Zr$_2$O$_7$ and Li$_2$O impurity phases, a potential capacitive contribution due to the nanoparticle nature of the active material (using similarly sized silica particles obtained from Ludox AS-40 as a model system, nominal particle size 22 nm, NH$_4^+$ counter ion), and a potential contribution from the Al current collector. Because some electrodes contained Super P carbon, we also carried out a control experiment with electrodes made only from Super P carbon and PVDF binder.

Fig. S29 shows the corresponding cell potentials as a function of time over multiple cycles and Fig. S30 shows the progression of capacity as a function of cycle number. For Li$_2$O/C prepared from lithium benzoate by a procedure analogous to that for the synthesis of Li$_8$ZrO$_6$/C, the voltage vs. time curves show highly symmetric triangular patterns of very short duration. These are typical for capacitive behavior (electric double-layer capacitance, dV/dt is constant), indicating that the carbon-coated Li$_2$O nanoparticles (grain size > 150 nm) store a small amount of charge on the surface. However, as is apparent from Fig. S30, the contribution of Li$_2$O relative to that of Li$_8$ZrO$_6$/C is negligible. Considering that the Li$_2$O content in the Li$_8$ZrO$_6$/C materials is also small, we rule out Li$_2$O as a significant contributor to the measured capacity. The aluminum, Ludox AS-40 silica, and Super P carbon cells show voltage vs. time patterns that are slightly less symmetric and less triangular than that of the Li$_2$O cell, with a small extent of curvature near the high potential during charge and the low potential during discharge. However, the patterns are still largely capacitive and capacity values are small compared to the capacity measured for Li$_8$ZrO$_6$/C under similar conditions (< 1.5% for Al, < 4.5% for Ludox AS-40 silica particles, and 3~5% for Super P carbon). Given that the grain size in Li$_8$ZrO$_6$ (30–90 nm) is larger than that of these silica particles and that the optimized Li$_8$ZrO$_6$/C cells did not contain any Super P carbon, we conclude that the capacitive contribution in the Li$_8$ZrO$_6$/C cells is very minor and not likely to be more than 5–11% of the total capacity at the discharge rates used in these tests. However, cyclic voltammetry experiments at varying voltage scan rates indicated that the capacitive contribution to charge storage in Li$_8$ZrO$_6$/C half cells increases at higher scan rates to 27% at 0.05 mV/s and 58% at 0.80 mV/s (supporting information Fig. S31 and S32, Table S7). This contribution results from the
small particle size of $\text{Li}_8\text{ZrO}_6$ in the composite electrodes and includes double-layer capacitance and pseudocapacitance through charge-transfer processes with surface atoms.

In contrast, $\text{Li}_6\text{Zr}_2\text{O}_7/\text{C}$ can be electrochemically cycled and provides significant capacity, as shown in Fig. S33. In fact, when the charge capacity limit was set to 221 mAh/g, this electrode material could maintain capacity over at least 50 cycles, similar to $\text{Li}_8\text{ZrO}_6$, with 100% Coulombic efficiency and less polarization than $\text{Li}_8\text{ZrO}_6$, indicated by a higher average discharge potential. Computed volume changes after removal of up to 2 Li/f.u. from $\text{Li}_6\text{Zr}_2\text{O}_7$ are very low and less than for $\text{Li}_8\text{ZrO}_6$, but the associated average voltages are higher, indicating that $\text{Li}_6\text{Zr}_2\text{O}_7$ is harder to delithiate (Table S8). After a drop in the first cycle from 2.78 to 2.34 V, the average discharge potential gradually increases with cycling to reach a value 2.56 V after 50 cycles. At cycle 50, the specific charge and discharge energies were 851 and 565 Wh/kg, respectively, with an energy efficiency of 66.4%. Given that the $\text{Li}_6\text{Zr}_2\text{O}_7$ content in the $\text{Li}_8\text{ZrO}_6$ materials is less than 4 wt%, the contribution of this phase should be negligible, unless more $\text{Li}_6\text{Zr}_2\text{O}_7$ is formed during charging. However, this electrode composition merits further investigation in the future.

The electrolyte used in these experiments was 1 M LiPF$_6$ in a 1:1:1 volume ratio of EC:DEM:DEC. To test its stability, fifteen cells containing $\text{Li}_8\text{ZrO}_6$:PVDF (90:10) were charged at a rate of $C/5$ and discharged at $C/10$ for fifteen cycles between 1.3 and 4.5 V with capacity limits set to 220 mAh/g. The combined electrolyte from these cells was dissolved in DMSO-$d_6$ and analyzed by $^1$H and $^{19}$F NMR spectroscopy. The spectra of the pristine electrolyte and of the recovered electrolyte after the fifteen cycles are shown in Fig. S36. On the basis of the $^1$H NMR spectra, the ratio of EC:DMC:DEC was maintained after cycling and no decomposition products were detected in these spectra. The $^{19}$F spectra also did not reveal any change in electrolyte composition after cycling. We can conclude that electrolyte decomposition, if any occurred during the 15 cycles, did not produce any new soluble products. A cyclic voltammogram of a half coin-cell also did not show any Faradaic current between 1.3 and 4.5 V that could be associated with electrolyte oxidation or reduction (Fig. S37). From this we conclude that most of the observed capacity was associated with the $\text{Li}_8\text{ZrO}_6$ material itself.
Figure S29. Charge and discharge curves for half-coin-cells containing (a) Li$_2$ZrO$_6$/C (90 Li$_2$ZrO$_6$/C : 10 PVDF), (b) Li$_6$Zr$_2$O$_7$/C (70 Li$_6$Zr$_2$O$_7$/C : 20 Super P carbon : 10 PVDF), (c) Li$_2$O/C (90 Li$_2$O/C : 10 PVDF), (d) Ludox AS-40 colloidal silica (70 silica : 20 Super P carbon : 10 PVDF), (e) an Al current collector (25 µm Al coated with carbon on both sides), and (f) Super P carbon (90 Super P carbon : 10 PVDF). All cells were cycled in the range from 1.3 to 4.5 V vs. Li/Li$^+$. Charge currents were ~ 0.02 mA and discharge currents ~0.01 mA except for Super P carbon. This corresponds to C/5 and C/10 charge and discharge rates for Li$_6$ZrO$_6$ ($C = 110.5$ mAh). For Super P carbon, charge and discharge rates were both C/5, based on Li$_6$ZrO$_6$. Note the different scales on the time axes.
Figure S30. Capacities of half-coin cells containing various electrode materials studied to estimate potential contributions of these materials to the observed capacity of the Li$_8$ZrO$_6$-containing cells. All cells were cycled in the range from 1.3 to 4.5 V vs. Li/Li$^+$ with charge currents ~0.02 mA and discharge currents ~0.01 mA unless noted otherwise below. This corresponds to $C/5$ and $C/10$ charge and discharge rates for Li$_8$ZrO$_6$ ($C = 110.5$ mAh).

Li$_8$ZrO$_6$/C-330 mAh/g limit: 90 Li$_8$ZrO$_6$/C : 10 PVDF, 1.0 mg Li$_8$ZrO$_6$ in the electrode. For the first 4 cycles at $C/5$ charge rate and $C/10$ discharge rate, a capacity restriction of 220 mAh/g was applied. Afterwards, the capacity restriction was raised to 330 mAh/g, the discharge rate was reduced to $C/15$ and the voltage limit removed. The cell maintained 100% Coulombic efficiency for 18 cycles until the voltage of the charging curve exceeded 4.7 V and evidence for electrolyte oxidation was observed in the form of spikes in the charging curve.

Li$_8$ZrO$_6$/C-220 mAh/g limit: 90 Li$_8$ZrO$_6$/C : 10 PVDF, 1.4 mg Li$_8$ZrO$_6$ in the electrode. A capacity restriction of 220 mAh/g was applied.

Li$_6$Zr$_2$O$_7$/C-220 mAh/g limit: 70 Li$_6$Zr$_2$O$_7$/C : 20 Super P carbon: 10 PVDF, 0.7 mg Li$_6$Zr$_2$O$_7$ in the electrode. A capacity restriction of 220 mAh/g was applied. The capacity drop after cycle 88 occurred when the upper voltage limit of 4.5 V was reached during charging. See also Figures S33 and S34.

Ludox AS-40: colloidal silica with particle size of ~22 nm, 70 silica : 20 Super P carbon: 10 PVDF, 1.0 mg silica in the electrode.

Super P carbon: 90 Super P carbon : 10 PVDF, 2.0 mg carbon in the electrode. Charge and discharge rates were both $C/5$, based on $C = 110.5$ mAh for Li$_8$ZrO$_6$.

Al: 25 µm Al current collector coated with carbon on both sides.

Li$_2$O/C: 90 Li$_2$O/C : 10 PVDF, 1 mg Li$_2$O in the electrode. Li$_2$O/C was synthesized from lithium benzoate by a procedure identical to that for the synthesis of Li$_8$ZrO$_6$/C, but without any zirconyl chloride. See also Figure S35.
Faradaic and capacitive contributions to charge storage in Li\textsubscript{8}ZrO\textsubscript{6}/C half cells.

The analysis of relative faradaic and capacitive contributions to charge storage in the Li\textsubscript{8}ZrO\textsubscript{6}/C half cells follows a procedure outlined by Wang et al. and Linström et al.\textsuperscript{15,16} The measured current ($i$) at different voltage scan rates ($v$) follows the relation:

\[ i = av^b \]  

(3)

where $a$ and $b$ are adjustable parameters. The limiting value $b = 0.5$ is associated with faradaic behavior due to Li-ion insertion according to equation 4:

\[ i = nFAC^*D^{1/2}v^{1/2} \left( \frac{\alpha nF}{RT} \right)^{1/2} \pi^{1/2} \chi(bt) \]  

(4)

The limiting value $b = 1$ corresponds to capacitive behavior according to equation 5:

\[ i = vC_dA \]  

(5)

$n$ = number of electrons involved in electrode reaction  
$F$ = Faraday constant  
$A$ = surface area of electrode materials  
$C^*$ = surface concentration of the electrode material  
$D$ = chemical diffusion coefficient  
$\alpha$ = transfer coefficient  
$R$ = molar gas constant  
$T$ = absolute temperature  
$\chi(bt)$ = normalized current for a completely irreversible system  
$C_d$ = capacitance

When both faradaic and capacitive contributions are present, the relative contributions are described by equation 6:
\[ i(V) = k_1v + k_2v^{1/2} \quad (6) \]

\( k_1v \) = current contributions from the surface capacitive effects

\( k_2v^{1/2} \) = current contributions from the diffusion-controlled intercalation process

Figure S31 shows the cyclic voltammetry curves for a Li\textsubscript{8}ZrO\textsubscript{6}/C:PVDF = 90:10 coin half-cell at various sweep rates. Values of \( b \) at the different voltages were calculated from the slopes of log \( i \) vs. log \( v \) plots (Figure S32). Finally, the % faradaic contributions from Li-ion insertion during discharge were estimated using equation 4 and the procedure outlined in the literature\textsuperscript{15} (Table S7).

Figure S31. Cyclic voltammetry curves for a Li\textsubscript{8}ZrO\textsubscript{6}/C:PVDF = 90:10 coin half-cell at the indicated sweep rates.

Figure S32. Plots of \( b \)-values vs. voltage for the positive scan (charging, left) and negative scan (discharging, right).
Comparison of charge-discharge curves for Li$_6$Zr$_2$O$_7$/C (top, electrode: 70 Li$_6$Zr$_2$O$_7$/C : 20 Super P carbon: 10 PVDF) and Li$_8$ZrO$_6$/C (bottom, electrode: 90 Li$_8$ZrO$_6$/C : 10 PVDF). These were charged at a charge rate of C/5 and discharge rate of C/10, with C = 110.5 mAh/g based on Li$_8$ZrO$_6$ for both samples. The cell containing Li$_6$Zr$_2$O$_7$/C shows stable cycling over at least 50 cycles. After a drop in the first cycle from 2.78 to 2.34 V, the average discharge potential gradually increases with cycling to reach a value 2.56 V after 50 cycles.
Figure S34. XRD patterns and compositions (estimated by Rietveld refinement) of samples with high content of Li₆Zr₂O₇ compared to a Li₈ZrO₆ sample. The synthesis of the sample with highest Li₆Zr₂O₇ content (blue) which was used for the electrochemical measurements, involved the preparation of nanosized ZrO₂ by confined calcination of ZrO(NO₃)₂ in Super P carbon black at 400 °C (2:1 C:Zr by mass) and then reacting this with lithium benzoate under nitrogen with a heating program of 1 °C/min to 600 °C, 2 h soak, 2 °C/min to 800 °C, followed by a 2 h soak time.
Figure S35. (a) Powder XRD pattern of the Li$_2$O product prepared by decomposition of lithium benzoate at 800 °C under nitrogen. Using the Scherrer equation and the peak at 66.6 °2θ, a grain size of 155 nm was calculated. (b) Thermogravimetric analysis trace of this material. The analysis was performed in air using a ramp rate of 10 °C/min from room temperature to 900 °C. The mass loss of 32 wt% between 400 and 600 °C is attributed to carbon in the material, which originated from the pyrolysis of the benzoate groups.
Electrolyte stability during cycling

Figure S36. (a) $^{19}$F NMR spectra and (b) $^1$H NMR spectra of the electrolyte before and after 15 charge and discharge cycles. (The peaks at -147.85 and -155.33 ppm in the $^{19}$F spectrum of the electrolyte after cycling are associated with the presence of BF$_4^-$, formed by the reaction of HF with the borate glass of the NMR tube.\textsuperscript{17})

Figure S37. Cyclic voltammogram of a Li$_8$ZrO$_6$/C coin half-cell with an electrode composition of 90 wt% Li$_8$ZrO$_6$/C and 10 wt% PVDF, using 1 M LiPF$_6$ in 1:1:1 (vol.) EC:DEM:DEC as the electrolyte. The scan rate was 0.1 mV/s.
Supplementary Tables

Table S1. Apparent room temperature Li-ion diffusion coefficients in Li$_x$ZrO$_6$ electrodes at different states of charge.

| $x$ in Li$_x$ZrO$_6$ | diffusion coefficient (cm$^2$/s) |
|---------------------|-----------------------------------|
| 8                   | 5.60x10^{-10}                    |
| 7.5                 | 4.02x10^{-12}                    |
| 7                   | 7.14x10^{-13}                    |
| 6.5                 | 7.55x10^{-14}                    |
| 6                   | 1.66x10^{-14}                    |
| 5.5                 | 5.38x10^{-13}                    |
| 5                   | 5.67x10^{-14}                    |
Table S2. The lattice constant, volume of the primitive unit cell, average voltage of Li$_x$ZrO$_6$ upon delithiation, computed by PBE+U (values in parentheses by HSE06).

|         | lattice constant (Å) | volume (Å$^3$) | volume change | average voltage (V vs. Li/Li$^+$) |
|---------|----------------------|----------------|---------------|----------------------------------|
| Li$_6$ZrO$_6$ | 6.037 (6.009)       | 133.26         |               |                                  |
| 6Li: 4-coordinated | 6.037 (6.009)       | (131.37)       |               |                                  |
| 2Li, 1Zr: 6-coordinated | 6.037 (6.009)      |               |               |                                  |
| Li$_7$ZrO$_6$ rem | 5.997 (5.958)       | 135.35         | +1.6%         | 2.98                             |
| 6Li: 4-coordinated | 5.849 (5.818)       | (133.22)       | +1.4%         | (4.04)                           |
| 1Li: 5-coordinated | 6.090 (6.056)       |               |               |                                  |
| Zr: 6-coordinated | 6.037 (6.009)       |               |               |                                  |
| Li$_6$ZrO$_6$ 12rem | 5.838 (5.806)       | 134.76         | +1.1%         | 2.96                             |
| 5Li: 4-coordinated | 6.306 (6.283)       | (133.0)        | +1.2%         | (3.93)                           |
| 1Li: 3-coordinated | 5.891 (5.870)       |               |               |                                  |
| Zr: 6-coordinated | 6.037 (6.009)       |               |               |                                  |
| Li$_6$ZrO$_6$ 157rem | 5.810 (5.782)       | 141.44         | +6.1%         | 3.13                             |
| 3Li: 4-coordinated | 5.689 (5.676)       | (139.48)       | +6.2%         | (3.45)                           |
| 2Li: 5-coordinated | 6.234 (6.205)       |               |               |                                  |
| Zr: 6-coordinated | 6.037 (6.009)       |               |               |                                  |
| Li$_7$ZrO$_6$ 1678rem | 6.580 (6.711)      | 134.27         | +0.8%         | 3.21                             |
| 2Li: 4-coordinated | 5.491 (5.325)       | (133.89)       | +1.9%         | (4.10)                           |
| 1Li: 5-coordinated | 5.801 (5.860)       |               |               |                                  |
| 1Li: 6-coordinated | 6.037 (6.009)       |               |               |                                  |
| Zr: 6-coordinated | 6.037 (6.009)       |               |               |                                  |
| Li$_6$ZrO$_6$ 23456rem | 6.217               | 140.00         | +5.1%         | 3.27                             |
| 3Li: 4-coordinated | 5.426               |               |               |                                  |
| Zr: 6-coordinated | 5.907               |               |               |                                  |
| Li$_7$ZrO$_6$ 245678rem | 5.733 (5.732)      | 110.14         | -17.3%        | 3.26                             |
| 2Li: 5-coordinated | 4.572 (4.501)       | (108.96)       | -17.1%        | (4.13)                           |
| Zr: 8-coordinated | 6.351 (6.361)       |               |               |                                  |
| LiZrO$_6$ 1245678rem | 6.123               | 128.91         | -3.3%         | 3.39                             |
| Li: 4-coordinated | 6.928               |               |               |                                  |
| Zr: 7-coordinated | 6.316               |               |               |                                  |
| ZrO$_6$          | 5.242 (4.695)       | 96.62          | -27.5%        | 3.64                             |
| Zr: 6-coordinated | 5.255 (4.642)       | (71.86)        | -45.3%        | (4.32)                           |
| (Zr: 10-coordinated) | 5.249 (4.629)       |               |               |                                  |
Notes for Table S2:

Positions of the Li atoms are identified in the inset of Fig. 2a. Li1 to Li6 correspond to Li atoms in tetrahedral sites, Li7 and Li8 to Li atom in octahedral sites. Average voltages vs. Li/Li⁺ were calculated using equation (1) on p. S-8. Several configurations of LiₓZrO₆ were calculated. The ones with the lowest energies are shown in this table. For LiₓZrO₆, the initial structure with two Li vacancies at tetrahedral sites and one at octahedral sites relaxed to the lowest energy. For LiₓZrO₆, the structure with two Li vacancies at tetrahedral sites and two at octahedral sites relaxed to the lowest energy. For LiₓZrO₆, the structure with five Li vacancies at tetrahedral sites relaxed to the lowest energy. For LiₓZrO₆, the structure with four Li vacancies at tetrahedral sites and two at octahedral sites relaxed to the lowest energy. For LiₓZrO₆, the structure with five Li vacancies at tetrahedral sites and two at octahedral sites relaxed to the lowest energy. The coordination numbers of Li and Zr after relaxation are listed in the first column. Any bond distance shorter than 2.5 Å is considered as coordination.

Crystallographic information files (.cif) for some of the relaxed LiₓZrO₆ structures (x = 8, 7, 6, 4) computed by HSE06 are provided as online files.
Table S3. Specific energy efficiencies and average discharge voltages of the cell described in Fig. 5a,b.

| cycle number | specific energy - charge (Wh/kg) | specific energy - discharge (Wh/kg) | energy efficiency (%) | average discharge voltage (V vs. Li/Li⁺) |
|--------------|----------------------------------|-------------------------------------|-----------------------|------------------------------------------|
| 1            | 747                              | 289                                 | 38.6                  | 2.00                                     |
| 2            | 722                              | 257                                 | 35.6                  | 2.06                                     |
| 3            | 743                              | 269                                 | 36.1                  | 2.11                                     |
| 8            | 811                              | 434                                 | 53.5                  | 2.17                                     |
| 9            | 863                              | 485                                 | 56.2                  | 2.20                                     |
| 10           | 857                              | 504                                 | 58.8                  | 2.28                                     |
| 20           | 863                              | 522                                 | 60.4                  | 2.36                                     |
| 30           | 820                              | 454                                 | 55.4                  | 2.06                                     |
| 40           | 811                              | 462                                 | 57.0                  | 2.09                                     |
| 50           | 792                              | 477                                 | 60.2                  | 2.16                                     |
| 60           | 670                              | 439                                 | 65.6                  | 1.99                                     |
| 70           | 663                              | 440                                 | 66.5                  | 1.99                                     |
| 80           | 683                              | 438                                 | 64.2                  | 1.98                                     |
| 90           | 703                              | 441                                 | 62.7                  | 1.99                                     |
| 100          | 703                              | 432                                 | 61.5                  | 1.96                                     |
Table S4. Impedance parameters calculated from the EIS spectra in Figure S19, using the equivalent circuit in Figure S21.

| state of charge | $R_1$ (Ω) | $Q_2$ (μF·s$^{a_2}$) | $\alpha_2$ | $R_2$ (Ω) | $Q_3$ (μF·s$^{a_3}$) | $\alpha_3$ | $R_3$ (Ω) | $Q_4$ (μF·s$^{a_4}$) | $\alpha_4$ | $\chi^2$ |
|----------------|-----------|----------------------|-----------|-----------|----------------------|-----------|-----------|----------------------|-----------|--------|
| 0 Li           | 4.5       | 4.19                 | 1.0       | 4.6       | 17.1                 | 0.74      | 224       | 8577                 | 0.64      | 1.16   |
| Cycle 1 - charge | 3.9     | 2.44                 | 1.0       | 3.3       | 46.9                 | 0.77      | 169       | 5170                 | 0.73      | 2.03   |
| Cycle 1 - full cycle | 3.8     | 5440                 | 1.0       | 90        | 138                  | 0.62      | 191       | 11790                | 0.42      | 2.59   |
| Cycle 2 - charge | 4.5     | 0.77                 | 1.0       | 7.2       | 96.1                 | 0.65      | 171       | 3260                 | 0.79      | 1.90   |
| Cycle 2 - full cycle | 8.8     | 0.85                 | 1.0       | 16        | 79.3                 | 0.63      | 337       | 1796                 | 0.80      | 0.67   |
| Cycle 3 - charge | 4.5     | 0.54                 | 1.0       | 24        | 28.7                 | 0.76      | 201       | 3487                 | 0.70      | 2.00   |
| Cycle 3 - full cycle | 5.7     | 0.73                 | 1.0       | 21        | 41.8                 | 0.69      | 326       | 1572                 | 0.72      | 1.23   |
| Cycle 4 - charge | 5.0     | 0.71                 | 1.0       | 8.9       | 80.1                 | 0.65      | 148       | 3850                 | 0.74      | 1.59   |
| Cycle 4 - full cycle | 5.3     | 0.75                 | 1.0       | 15        | 57.2                 | 0.66      | 275       | 1942                 | 0.66      | 1.68   |
| Cycle 5 - charge | 7.2     | 0.54                 | 1.0       | 21        | 29.2                 | 0.71      | 170       | 3256                 | 0.68      | 0.71   |
| Cycle 5 - full cycle | 8.2     | 0.82                 | 1.0       | 22        | 37.2                 | 0.67      | 329       | 1473                 | 0.75      | 0.56   |

**Notes:** $\alpha$ is the phase angle of the constant phase element $Q$ in radians ($0 < \alpha < 1$). When $\alpha$ is close to 0, the constant phase element $Q$ resembles a resistor. When $\alpha$ is close to 1, $Q$ resembles a capacitor. $\chi^2$ is an indication of goodness of fit. For these data, a coin cell was charged to remove 1 Li/f.u. and discharged for 5 cycles each.
Table S5. Impedance parameters obtained by fitting the EIS spectra in Figure S20, using the equivalent circuit in Figure S21 and the Z-Fit function of the EC-lab impedance fitting tool.

| state of charge | \( R_1 \) (Ω) | \( Q_2 \) (µF·s\(^{-1}\)) | \( \alpha_2 \) | \( R_2 \) (Ω) | \( Q_3 \) (µF·s\(^{-1}\)) | \( \alpha_3 \) | \( R_3 \) (Ω) | \( Q_4 \) (µF·s\(^{-1}\)) | \( \alpha_4 \) | \( \chi^2 \) |
|-----------------|----------------|-------------------|----------------|----------------|-------------------|----------------|----------------|-------------------|----------------|----------------|
| 0 Li             | 4.5            | 4.19              | 1.0            | 4.6            | 17.1              | 0.74           | 224            | 8577              | 0.64           | 1.16           |
| 1 Li - charge    | 3.9            | 2.44              | 1.0            | 3.3            | 46.9              | 0.77           | 169            | 5170              | 0.73           | 2.03           |
| 1 Li - full cycle| 3.8            | 5440              | 1.0            | 89.8           | 138              | 0.62           | 191            | 11790             | 0.42           | 2.59           |
| 2 Li - charge    | 5.2            | 11.3              | 1.0            | 188            | 6.2               | 0.76           | 214            | 2612              | 0.66           | 1.37           |
| 2 Li - full cycle| 5.1            | 3.59              | 1.0            | 13.4           | 18.1              | 0.67           | 656            | 1065              | 0.70           | 1.55           |
| 3 Li - charge    | 5.9            | 5.01              | 0.80           | 141            | 16.1              | 0.81           | 1714           | 1889              | 0.70           | 1.06           |
| 3 Li - full cycle| 5.4            | 5.02              | 0.80           | 150            | 20.5              | 0.80           | 2010           | 4555              | 0.75           | 1.28           |

As shown in Table S4, when a cell was charged to remove 1 Li/f.u. and then discharged, for 5 cycles each, the value of \( R_1 \) (electrolyte resistance) remained approximately constant after each charge/discharge cycle. At this level of charge, the value of the charge-transfer resistance (\( R_3 \)) tended to decrease after the cell was charged and increase after the cell was discharged. However, when half-cells were charged more deeply (up to 3 Li/f.u., Table S5) and then discharged, the value of the charge transfer resistance increased with depth of charge, with a particularly large jump between 2 and 3 Li/f.u. The value of the electrolyte resistance \( R_1 \) continued to remain approximately constant after each charge/discharge cycle.
Table S6. Specific energy efficiencies and average discharge voltages of the cell described in Figure S18 for selected cycles.

| cycle number | specific energy - charge (Wh/kg) | specific energy - discharge (Wh/kg) | energy efficiency (%) | average discharge voltage (V vs. Li/Li⁺) |
|--------------|----------------------------------|-------------------------------------|-----------------------|------------------------------------------|
| 10           | 1273                             | 733                                 | 57.5                  | 2.21                                     |
| 15           | 1348                             | 763                                 | 56.6                  | 2.31                                     |
| 21           | 1397                             | 820                                 | 58.7                  | 2.48                                     |
| 22           | 1254                             | 769                                 | 61.3                  | 2.57                                     |

Table S7. Relative faradaic contributions from Li-ion insertion during discharge of a Li₃ZrO₆/C:PVDF = 90:10 coin half-cell at the indicated sweep rates.

| scan rate (mV/s) | % faradaic contribution from Li-ion insertion during discharge |
|------------------|---------------------------------------------------------------|
| 0.05             | 73                                                            |
| 0.10             | 66                                                            |
| 0.20             | 59                                                            |
| 0.40             | 50                                                            |
| 0.80             | 42                                                            |
Table S8. The energy, unit cell volume, and average voltage of Li$_x$Zr$_4$O$_{14}$ (representative of Li$_6$Zr$_2$O$_7$) upon partial delithiation, computed by PBE+U.*

| PBE+U, U = 6.0 eV | energy (eV) | volume (Å$^3$) | average voltage (V vs. Li/Li$^+$) |
|-------------------|-------------|----------------|----------------------------------|
| Li$_{12}$Zr$_4$O$_{14}$ | -143.706    | 313.58         |                                 |
| Li$_{11}$Zr$_4$O$_{14}$ (Li12 removed) | -138.131    | 313.96         | 3.67                             |
| Li$_{10}$Zr$_4$O$_{14}$ (Li12, Li6 removed) | -133.017    | 313.23         | 3.44                             |
| Li$_8$Zr$_4$O$_{14}$ (Li6, Li7, Li9, Li12 removed) | -122.424    | 313.18         | 3.42                             |

*Atom numbers are shown in the structure below (space group C2/c).

Table S9. Properties of Li$_8$ZrO$_6$ compared to other commercial cathode materials for LIBs.

| cathode material | molar mass (g/mol) | spec. cap. (theor. 1 Li) (m Ah/g) | spec. cap. (actual Li) (m Ah/g) | ave. voltage (V) | specific energy (Wh/kg) | dens. vol. energy density (g/cm$^3$) (Wh/L) |
|------------------|--------------------|-----------------------------------|---------------------------------|-----------------|--------------------------|-----------------------------------------------|
| LiCoO$_2$ (LCO)  | 97.87              | 274                               | 140                             | 3.9             | 546                      | 5                                            | 2730                                          |
| LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) | 96.5               | 272                               | 160–170                        | 3.8             | 610–650                  | 4.7                                          | 2867–3055                                     |
| LiFePO$_4$ (LFP) | 157.76             | 170                               | 150–170                        | 3.45            | 518–587                  | 3.6                                          | 1864–2113                                     |
| LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) | 96.09              | 279                               | 180–200                        | 3.8             | 680–760                  | 4.45                                         | 3026–3382                                     |
| Li$_8$ZrO$_6$, 2 Li | 242.75             | 221                               | 221                            | 2.0–2.4        | 442–530                  | 3                                            | 1326–1590                                     |
| Li$_8$ZrO$_6$, 3 Li | 242.75             | 331                               | 331                            | 2.2–2.6        | 728–861                  | 3                                            | 2184–2583                                     |

Notes: For LCO, NMC, LFP and NCA, data are taken from reference$^{18}$. All values ignore masses or volumes of the electrolyte, solvent, current collectors and casing.
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