High-performance K-ion half/full batteries with superb rate capability and cycle stability

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Currently, a big problem for exploring K-ion half/full batteries is how to bring them with both high specific capacity and long cycling stability simultaneously, in terms of their intrinsically sluggish kinetics of K\textsuperscript{+} with larger radius than that of Li\textsuperscript{+}, which often causes huge volume change over the electrochemical reaction. Herein, we report the exploration of high-performance K-ion half/full batteries with superb rate capability and cycle stability based on B-doped porous carbons with increased active sites and improved conductivity. The as-assembled K-ion half cell exhibits an excellent rate capability of 428 mA h g\textsuperscript{-1} at 100 mA g\textsuperscript{-1} and a high reversible specific capacity of 330 mA h g\textsuperscript{-1} with 120% specific capacity retention after 2,000 cycles at 2,000 mA g\textsuperscript{-1}, which is state of the art among those based on carbon materials. Moreover, the as-constructed full cell delivers 98% specific capacity retention over 750 cycles at 500 mA g\textsuperscript{-1}, which is superior to most of the analogs based on carbon materials that have been reported thus far, underscoring their potential applications in advanced energy storage.

B-doping | carbon materials | K-ion batteries | specific capacity | cycle stability

Currently, lithium-ion batteries (LIBs) have been widely applied in various electronics and electric vehicles, in respect to their high energy densities with long cycling lifetimes (1–3). However, the development of LIBs is fundamentally hampered by the intrinsic lack of Li resources, as well as the high cost of Li. Accordingly, there are some typical emerging candidates as promising alternatives to LIBs, including Na-ion batteries (4, 5), Al-ion batteries (6), and Mg-ion batteries (7). Among these, K-ion batteries (KIBs) hold some unique and exciting merits, making them an interesting alternative to LIBs. Firstly, compared to Li, there are many more resources of K in the earth’s crust (2.09 wt% vs. 0.0017 wt% of Li) (8). Secondly, the standard potential of K/K\textsuperscript{+} is ~2.94 V, which is lower than those of Na/Na\textsuperscript{+} (~2.71 V) and Li/Li\textsuperscript{+} (~2.79 V) in propylene carbonate (9). Thirdly, the K\textsuperscript{+} ion has better ionic conductivity than its Li\textsuperscript{+} and Na\textsuperscript{+} counterparts due to its weaker Lewis acidity with smaller solvated ions, thus endowing the desired high rate capability (10). Moreover, the exploration of KIBs could use Al foil instead of Cu foil as the current collectors, implying their remarkably reduced cost (11). Finally, the KIBs hold the most interesting advantage in that they can use graphite for anode electrodes with a high specific capacity of ~273 mA h g\textsuperscript{-1} (12). However, the development of KIBs is still fundamentally limited by the intrinsically sluggish kinetics of K\textsuperscript{+} with larger radii (1.38 Å) than those of Na\textsuperscript{+} (1.02 Å) and Li\textsuperscript{+} (0.76 Å), which is recognized as a big problem for exploring K-ion half/full batteries with long cycling stability.

To overcome this point, to date, the metals/alloys, metal phosphides/oxides/sulfides, and carbon materials were widely investigated as the electrodes for potassium storage (13–16). Among them, the porous carbons are considered the most popular owing to their advantages of low cost, nontoxicity, good conductivity, elastic framework, and rich porosity, which could not only avoid the structure damage caused by the intercalation/de-intercalation of the K\textsuperscript{+} ions with large radius, but also facilitate the infiltration of electrolyte and the diffusion of K\textsuperscript{+} (17). Moreover, heteroatom doping—including F, N, S, O, P, and B has been proposed as another effective way to enhance the electrochemical performance of carbonaceous materials (18–21). For instance, Guo et al. reported N/S codoped graphene nanosheets for KIBs, which had a specific capacity of 251 mA h g\textsuperscript{-1} at 100 mA g\textsuperscript{-1} with 81% specific capacity retention after 100 cycles and 188.8 mA h g\textsuperscript{-1} at 1,000 mA g\textsuperscript{-1} with 78.4% specific capacity retention after 2,000 cycles (19). Wang et al. reported N/P codoped hollow porous carbons for KIBs, which had a specific capacity of 205.2 mA h g\textsuperscript{-1} at 2,000 mA g\textsuperscript{-1} with 88% specific capacity retention after 1,000 cycles (21). Lian et al. reported B/O codoped carbon for KIBs, which exhibited a specific capacity of 215.7 mA h g\textsuperscript{-1} at 500 mA g\textsuperscript{-1} with 58.9%
specific capacity retention over 200 cycles and 119.4 mA h g\(^{-1}\) at 1,000 mA g\(^{-1}\) with 34.1% specific capacity retention after 500 cycles (22). However, it is still a grand challenge for exploring advanced KIBs with high specific capacity and long cycle stability in the meantime (23).

Herein, we report the exploration of high-performance K-ion half/full batteries with both superb rate capability and cycle stability based on B-doped porous carbons (BPC). They are fabricated via a facile freeze-drying followed by annealing with the assistance of NaCl as the pore creation agent. It is evidenced that the resultant BPC could improve the interface interaction and facilitate the infiltration of electrolytes with enhanced K\(^+\) diffusion. Moreover, the incorporated B dopants would introduce the active sites with improved conductivity for the electrode. As a proof of concept, the as-assembled K\(^+\) half/full batteries exhibit an excellent rate capability of 428 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) and a high reversible specific capacity of 330 mA h g\(^{-1}\) after 2,000 cycles at 2,000 mA g\(^{-1}\), which is the best among those based on carbon materials. Moreover, the as-constructed full cells deliver 98% specific capacity retention after 750 cycles at 500 mA g\(^{-1}\), which is superior to most of those based on carbon materials for potassium storage reported thus far, representing their promising practical applications.

Results and Discussion

Fig. 1 A–C shows the typical scanning electron microscope (SEM) images of as-synthesized B-doped carbons under different magnifications, representing their hierarchically porous structures. The obtained B-doped porous carbons are referred to as sample BPC. For comparison, the microstructures of the product without doping are provided in SI Appendix, Fig. S1, representing their also-porous-characteristic; they are referred to as sample pure porous carbons (PC). Fig. 1D shows the typical transmission electron microscope (TEM) image, further evidencing the porous nature of sample BPC (SI Appendix, Fig. S2A). Fig. 1E and SI Appendix, Fig. S2B, give the corresponding high-resolution TEM (HRTEM) images of sample BPC, disclosing their amorphous characteristic and agreeing on the recorded selected area electron diffraction (SAED) pattern given as the top-right inset in Fig. 1E. The disordered lattice fringes imply a low degree of graphitization. The Raman spectra of sample BPC (Fig. 1F) and PC (SI Appendix, Fig. S3) display two peaks at \(\sim\)1,330 (disorder/defect-induced D band) and 1,680.7 cm\(^{-1}\) (in-plane vibrational G band), respectively. Accordingly, the \(I_D/I_G\) is approximately 0.96, which is higher than that of the PC (\(I_D/I_G = 0.89\)). The high \(I_D/I_G\) value implies that sample BPC have more active sites with lower degrees of graphitization than sample PC, which is beneficial for the electrochemical performance of the batteries. Fig. 1 G–I are the typical element mappings, representing the uniform spatial distribution of the incorporated B dopants.

SI Appendix, Fig. S4A, provides the representative X-ray diffraction (XRD) pattern of the products. The observed weak diffraction peak at (101) plane indicates the low degree of graphitization. The one at (002) plane of the sample BPC shifts to a lower degree as compared to that of the sample PC, demonstrating that the interspace of the sample BPC is larger than that of the sample PC. This verifies that the introduced B dopants could expand the interlayer spacing, which is beneficial for the insertion/extraction of K\(^+\) ions during the charging/discharging process. SI Appendix, Figs. S4B and S5A, depict the isotherm curves of sample BPC and PC, both of which demonstrate a typical II type isotherm behavior with H3 hysteresis, further confirming their porous characteristics. The Brunner–Emmet–Teller surface area and pore volume of the sample BPC are \(\sim\)400.54 m\(^2\) g\(^{-1}\) and \(\sim\)1.18 cm\(^3\) g\(^{-1}\), and those of the sample PC are \(\sim\)476.49 m\(^2\) g\(^{-1}\) and \(\sim\)0.428 cm\(^3\) g\(^{-1}\), respectively. The pore size distribution (SI Appendix, Fig. S4C) shows the existence of mesopores sized from 2 to 5 nm within the BPC, which could improve the ion adsorption and shorten the diffusion distance, thus enhancing the charging/discharging process (24). As for the sample PC, it is mainly composed of mesopores (SI Appendix, Fig. S5B). SI Appendix, Fig. S4D, provides the typical X-ray photoelectron spectroscopy (XPS) survey spectra, revealing that sample BPC contains 3.85 and 96.15 at% of B and C, respectively. In contrast, the PC without doping contains only C (SI Appendix, Fig. S5C). In the high-resolution C1 spectra (SI Appendix, Fig. S4E), the peaks at 284.7, 285.5, and 288 eV are assigned to the C-C, C-O/C-O-B (25), and C = O (26) bonds, respectively, evidencing the formation of B-doped carbons. The high-resolution B1 XPS spectrum can be deconvoluted into two types of B species (SI Appendix, Fig. S4F), which are located at 191.5 and 192.7 eV and are attributed to the B-C (27) and BCO\(_2\) (28) bonds, respectively. The deconvolution of C1 spectra located at 284.7, 285.5, and 288 eV of the sample PC (SI Appendix, Fig. S5D) is ascribed to the binding energies of C-C, C-O (25), and C = O (26) bonds, respectively.

Fig. 2A shows the cyclic voltammetry (CV) of the sample BPC at a scan rate of 0.2 mV s\(^{-1}\). In the first cycle, there is an irreversible and large cathodic peak at \(\sim\)0.75 V, indicating the decomposition of electrolyte accompanied by the formation of solid electrolyte interface films (29). The spikelike peak at \(\sim\)0.05 V implies that the K\(^+\) has been intercalated into the carbon layers with the formed K-intercalated compounds. In the anodic curves, the detected broad oxidation peak at \(\sim\)0.45 V during the charging process represents the extraction of K\(^+\) from the BPC. Moreover, the nearly overlapping cathodic/anodic peaks after first cycle demonstrate the high cycle stability with tiny polarization of the electrode based on the sample BPC. As shown in SI Appendix, Fig. S6A, the CV curve of the sample PC is similar to that of the sample BPC, with an irreversible cathodic peak at \(\sim\)0.75 V. SI Appendix, Figs. S6B and S7A, provide the charge/discharge curves of the sample PC and BPC with different cycles between 0.01 and 3.0 V at a current density of 100 mA g\(^{-1}\). It seems that the discharge-charge-specific capacities of the sample BPC are higher than those of the PC, in respect to each cycle. Both samples exhibit an irreversible platform over the first discharge curve, consistent with the CV analyses, thus favoring lower initial coulombic efficiencies (ICEs; <40%). Moreover, their rate performances are recorded, as shown in Fig. 2B and SI Appendix, Fig. S6C, respectively. It discloses that the sample BPC exhibits high specific capacities of 428, 375, 350, 340, and 315 mA h g\(^{-1}\) at the current densities of 100, 200, 300, 500, and 1,000 mA g\(^{-1}\), respectively, which are superior to those of the sample PC (i.e., 280, 210, 200, 150 and 150 mA h g\(^{-1}\) at 100, 200, 300, 500, and 1,000 mA g\(^{-1}\), respectively). Furthermore, when the current density returns to 100 mA g\(^{-1}\), the specific capacity retention of the sample BPC could be 95%, which is also higher than that of the sample PC (82%), underscoring its excellent structural stability and rate performance (see Fig. 2C) (18, 20, 29–45). The cycling performances of the sample BPC and PC under different current densities are presented in Fig. 2 D and E and SI Appendix, Fig. S6 D and E, respectively. It seems that under the low current density of 100 mA g\(^{-1}\), both of them have good cycle stability. However, when applied under high current density, the specific capacity retention of the sample BPC could be up to
120%, better than that of the sample PC (~98%). Notably, after running 2,000 cycles, the sample BPC still delivers a high specific capacity of 330 mA h g$^{-1}$ under 2,000 mA g$^{-1}$, illustrating its totally superior electrochemical performance to those ever reported. The achieved high specific capacity and cycle stability might be mainly attributed to the fact that the sample BPC could be fully activated by the electrochemical reaction with more exposed active sites, consistent with the Raman characterizations. It suggests that the ID/IG of the sample BPC after cycling is approximately 0.99, which is higher than that before cycling (ID/IG $= 0.96$; Fig. 1F). In addition, the sample BPC exhibits high coulombic efficiencies, except for the ICE, implying its potential toward practical applications. Moreover, after 5,000 cycles under an ultrahigh current density of 3,000 mA g$^{-1}$, the sample BPC still exhibits a high specific capacity of 175 mA h g$^{-1}$, further representing its excellent cycling performance.

To understand the energy storage mechanism and reaction kinetics, the CV profiles are measured in the voltage range of 0.01 to 3.0 V at different scan rates. As shown in Fig. 3A, the shape of CV curves is well maintained with small overpotential and becomes broader as the scan rates are increased from 0.2 to 1 mV s$^{-1}$, suggesting that the K$^+$ storage should be dominated by the capacitive behaviors. The following equation could determine whether there is a pseudocapacitive behavior over the charge/discharge processes or not:

$$i = av^b$$

where $i$ is the peak current, $v$ is the scan rate, and $a$ and $b$ are the adjustable parameters. Accordingly, $b$ could be acquired from the slope by plotting log($i$) against log($v$). Generally, once $b = 0.5$, the electrode should be dominated by the solid-state diffusion process. Once $b = 1$, it undergoes capacitance activities; once the value of $b$ is between 0.5 and 1, it exhibits mixed battery and capacitance behaviors. In the current case, the sample BPC shows a good linear relationship between log($i$) and log($v$) with the $b$ values of approximately 0.996 and 0.7 for anodic and cathodic peaks, respectively. It suggests that the K$^+$ storage should be dominated by the capacitive process accompanying the diffusion procedure, thus favoring the desired cycle stability and rate performance. The contribution of capacitance at a given scan rate can be calculated by the following:

$$\frac{i(V)}{v^{1/2}} = k_1v^{1/2} + k_2$$

where $v$ is the specific voltage scan rate, $V$ is the specified voltage, and $k_1$ and $k_2$ are the adjustable parameters. Based on the
purple-highlighted area in Fig. 3C, the sample BPC shows a capacitive contribution of 78.9% at the given scan rate of 0.6 mV s\(^{-1}\). With the raise in scan rates, the capacitive contribution increases from 67.86 to 84% (Fig. 3D), further confirming that the K\(^+\) storage should be driven mainly by the surface capacitive behaviors. To understand the origin of the electrochemical performance, the galvanostatic intermittent titration technique (GITT) method (Eq. 3) is applied to investigate the K\(^+\) diffusion coefficients, as shown in Fig. 3E and F and SI Appendix, Fig. S8:

\[
D = \frac{4}{\pi \tau} \left( \frac{m_B V_M}{M_B S} \right)^2 \left( \frac{\Delta E_S}{\Delta E_T} \right)^2
\]

where \(\tau\) is the duration of the current pulse, \(m_B\) is the mass loading of the electrode material, \(S\) is the area of the electrode, \(\Delta E_T\) is the potential difference during the current pulse, \(\Delta E_S\) is the quasi-thermodynamic equilibrium potential difference between before and after the current pulse, \(V_M\) represents the molar volume of the materials, and \(M_B\) is the molar mass of carbon. Correspondingly, the value of \(M_B V_M\) can be obtained (21):

\[
\frac{M_B}{V_M} = \rho = \frac{1}{V_{\text{total}} + \frac{1}{\rho_{\text{carbon}}}}
\]

where \(\rho\) (g cm\(^{-3}\)) is the density of the materials, \(V_{\text{total}}\) (cm\(^3\) g\(^{-1}\)) is the total pore volume measured from the N\(_2\) isotherm, and \(\rho_{\text{carbon}}\) is the true density of carbon. It shows that the diffusions of the sample BPC and PC exhibit the same trend, implying that both of them behave similarly to the K\(^+\) storage mechanism. As compared to the sample PC, the sample BPC has higher diffusion coefficients in the potassiation and depotassiation processes (Fig. 3F and SI Appendix, Fig. S8B), indicating the faster reaction kinetics of K\(^+\), thus responsible for enhanced rate performance of the sample BPC.

To further demonstrate the electrochemical behaviors, the electrochemical impedance spectroscopies (EIS) of the sample BPC and PC before and after 100 cycles at 2,000 mA g\(^{-1}\) are investigated, as shown in Fig. 3G and H and SI Appendix, Fig. S9, respectively. They disclose that the diameters of EIS semicircles of the BPC are smaller than those of the sample PC before and after cycles, indicating the fundamentally enhanced electron transmission of the sample BPC. Moreover, it seems that the EIS semicircle becomes smaller after 100 cycles, evidencing that the resistance has been reduced with the K\(^+\) intercalation, responsible for the observed ultrahigh stability (19). Furthermore, the recorded TEM (SI Appendix, Figs. S10 and S11), HRTEM (SI Appendix, Fig. S10D) images, and elemental mappings (SI Appendix, Fig. S11) of the sample BPC after 100 cycles at 2,000 mA g\(^{-1}\) show nearly no change over the cycling process (SI Appendix, Fig. S10A), reflecting its robust structure for high cycle stability. Notably, the interlayer spaces of the sample BPC before and after the cycles are bigger than those of pure graphene (~0.364 nm), demonstrating that the incorporated B dopants could expand the interlayer spacing, consistent with the XRD characterizations (SI Appendix, Fig. S4).
The coordination numbers of B are often unsaturated, suggesting the existence of lone pair electrons. Accordingly, the repulsion of lone pair electrons increases the distance between B-doped graphene sheets. Based on the discussion above, a schematic diagram is proposed to illustrate the potassium storage mechanism (Fig. 3). Firstly, the B dopants could introduce increased active sites for absorbing more K\(^+\) for energy storage and form a stable B-C chemical bond to limit the structural damage. Also, the B dopants can increase the number of hole-type charge carriers, thereby enhancing the conductivity of the electrode (48). Secondly, the hierarchically porous carbon layer structure (SI Appendix, Fig. S4C) could facilitate the insertion of K\(^+\) ions with improved adsorption and shortened diffusion distance, thus favoring the totally enhanced charging/discharging process.

To show the potential application for energy storage, the K\(^+\) full cell is constructed with the sample BPC and potassium Prussian blue materials (KPBs) as the anode and cathode, respectively (Fig. 4). To eliminate the initial irreversible specific capacity and compensate enough K\(^+\) for energy storage and form a stable B-C chemical bond to limit the structural damage. Also, the B dopants can increase the number of hole-type charge carriers, thereby enhancing the conductivity of the electrode (48). Secondly, the hierarchically porous carbon layer structure (SI Appendix, Fig. S4C) could facilitate the insertion of K\(^+\) ions with improved adsorption and shortened diffusion distance, thus favoring the totally enhanced charging/discharging process.

Conclusions. In summary, we reported the exploration of high-performance half/full batteries with both superb rate capability and cycle stability based on BPC, which are fabricated by a facile freeze-drying followed by annealing treatment with NaCl as the pore creation agent. The as-assembled K\(^+\) half batteries exhibit an excellent rate capability of 428 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) and a high reversible specific capacity of 330 mA h g\(^{-1}\) after 2,000 cycles at 2,000 mA g\(^{-1}\), which is the best among those based on carbon materials. The as-constructed full cells deliver 98% specific capacity retention after 750 cycles at 500 mA g\(^{-1}\), superior to the typical K-ion full cells reported thus far (SI Appendix, Table S2).
mainly attributed to the as-fabricated BPC, which could facilitate the infiltration of electrolyte with enhanced K\textsuperscript{+} diffusion kinetics, as well as increased active sites and improved conductivity. The present work might give some insight into exploring advanced anode materials for K\textsuperscript{+} batteries with ultrahigh stability and high specific capacity toward practical applications.

Materials and Methods

Material Synthesis.

Preparation of the BPCs and PCs. In a typical process, 0.012 M citric acid monohydrate (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}·H\textsubscript{2}O, Aladdin), 0.0208 M boric acid (H\textsubscript{3}BO\textsubscript{3}, A.R, Aladdin), and 10 g sodium chloride (NaCl, Aladdin) were dissolved into 60 mL deionized (DI) water and subjected to magnetic stirring to obtain homogeneous dispersion. Subsequently, the resultant solution was freeze-dried at −80 °C and then subjected to high-temperature carbonization by maintaining at 750 °C for 2 h under argon environment. Afterward, the residual sodium chloride was washed by DI water. Subsequently, the product was collected by centrifugation and then subjected to drying at 80 °C for 2 h under argon environment. Afterward, the residual sodium chloride was washed by DI water. Subsequently, the product was collected by centrifugation and drying under −80 °C for obtaining the target BPC. For comparison, PC without doping were also prepared with similar experimental process, except for the use of boric acid for introducing B dopants.

Preparation of KPBs. As for the preparation of KPBs, 0.001 M K\textsubscript{4}Fe(CN)\textsubscript{6} was first dissolved into 160 mL DI water, which was designated “solution A.” Afterward, 0.002 M FeCl\textsubscript{3} was dissolved into 40 mL DI water, and the resultant product was referred to as “solution B.” Subsequently, solution B was added drop by drop into solution A under magnetic stirring for obtaining homogeneous dispersion, followed by aging for 24 h. Finally, the powders were washed and centrifugated with ethanol/DI water and subjected to drying at 80 °C over night.

Microstructural Characterization. The crystal structures were analyzed by XRD with CuK\textalpha\ radiation (λ = 1.5406 Å) (X’pertro, Philips, Germany). The microstructures and morphology were investigated by field emission SEM (S4800, Hitachi, Japan) and HRTEM (JEM-2100F, JEOL, Japan) equipped with energy-dispersive X-ray spectroscopy (Quantax-STEM, Bruker, Germany). The Raman spectrum (XploRA PLUS, HORIBA, France) with frequencies ranging from 500 to 2500 cm\textsuperscript{−1} was tested at room temperature (RT). The specific surface area and pore distribution were determined by N\textsubscript{2} adsorption at −195.8 °C on an analyzer (Micromeritics, ASAP 2020M, USA). The XPS (ES-CALAB 250i, Thermo Fisher Scientific, America) was used to investigate the surface elemental chemical state of the product under RT.

Electrochemical Measurements. For preparing the anode electrode, 80 wt% of as-prepared active material, 10 wt% carbon blacks, and 10 wt% sodium carboxymethyl celluloses (A.R., 99%, Aladdin) were milled together and dispersed into a mixed solution of DI water and ethanol with a mass ratio of 4:1. The total mass of DI water and ethanol is fixed at 20 times to the active material. After stirring for 8 h, the mixed slurries were coated onto a copper foil and cut into discs with diameters of 12 mm after drying at 80 °C for 12 h. The active material mass loading of the electrodes was fixed in the range between 0.8 and 1.8 mg cm\textsuperscript{−2}. For the preparation of cathode electrode, 70 wt% KPB materials, 20 wt% carbon blacks, and 10 wt% polyvinylidene fluoride (A.R., 99%, Aladdin) were milled together with N-methyl-2-pyrrolidone as the solvent. The total mass of solvent is fixed at 10 times to the KPB counterpart. After stirring for 20 h, the mixed slurries were coated onto Al foil, which was then cut into discs with diameters of 12 mm after drying at 80 °C for 12 h. The active material mass loading of the cathode electrodes was fixed in the range from 0.6 to 1.0 mg cm\textsuperscript{−2}. Then, the batteries were assembled into 2032 button battery in a glove box under Ar protection. For K\textsuperscript{+} half batteries, the potassium was used as the counter electrode. For K\textsuperscript{+} full batteries, the BPC or PC electrode and KPB electrode were used as anode and cathode, respectively. 3M bisfluorosulfonylimide potassium in ethylene glycol dimethyl ether and glass fiber (Whatman GF/F) were used as the electrolyte and separator for K\textsuperscript{+} half/full batteries, respectively. The electrochemical performance was measured on the Neware BTS-CT-3008-TC system. The CV measurements were tested on Chenhua CHI660E electrochemical workstation, with a scan rate of 0.2 mV s\textsuperscript{−1} at potentials ranging from 0.01 to 3.0 V. The EIS spectrum was tested on Chenhua CHI660E electrochemical workstation with frequencies ranging from 0.1 to 100 KHz under RT.

Data Availability. All study data are included in the article and/or SI Appendix.

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