Highly stable cycling of a lead oxide/copper nanocomposite as an anode material in lithium ion batteries†

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Nanostructured composites of lead oxide/copper–carbon (PbO/Cu–C) were synthesized through in situ solvothermal synthesis and heat treatment of PbO/Cu with polyvinyl pyrrolidone (PVP) and used as lithium-ion battery anodes. A PbO active particle was embedded in the Cu and PVP–C matrix, accommodating volume changes and maintaining the electronic conductivity of PbO. The composite exhibits a superior electrochemical performance, with a capacity of 420 mA h g⁻¹ at a current density of 165 mA g⁻¹, compared with previously reported Pb and PbO composite anodes. The developed anode exhibits >90% capacity retention after 9500 cycles, beginning from the second cycle, at a current density of 5.5 A g⁻¹.

1. Introduction

Worldwide energy consumption has extensively increased in the twenty-first century, and research is increasingly focusing on energy source technologies with environmental considerations, such as natural energy sources, nuclear energy, fuel cells, and batteries.¹ Lithium-ion batteries (LIBs) are highly promising devices for supplying power to small electronic devices because of their flexible design, high energy density, and long lifespan.² However, with the rapid development in electronics and increasing focus on renewable energy, high-performance electrode materials are required to meet the increasing demands for high energy density, large gravimetric and volumetric capacities, and high cycle performance.³ Accordingly, substantial research efforts have been devoted to various LIB electrode materials. Among them, metal oxides are exceptional anodes because of their high theoretical capacity and low cost. Metal oxides usually exhibit low volume changes during cycling, and the first lithiation forms metal clusters surrounded by lithium oxides and lithium metal alloys that act as buffer layers for accommodating the cyclic volume changes, thus possibly enhancing cycling performance. Several studies have reported metal-oxide-based carbon composites with long cycle lives. For example, Li et al. reported the one-step hydrothermal synthesis of Nb₂O₅/carbon composites with enhanced electrochemical performance (specific capacity = 100 mA h g⁻¹ at a current density of 500 mA g⁻¹).⁴ Wang et al. fabricated carbon-supported porous TiO₂ through multiple sol–gel processes and subsequent carbonization and realized improved cycling performance and an excellent rate capability of up to 10 C.⁵ Liu et al. prepared mesoporous core/shell structured SnO₂/C nanocomposites through facile vacuum-assisted impregnation using SBA-15 as a hard template and reported high specific capacity and excellent high-rate performance (510 mA h g⁻¹ at 10 A g⁻¹).⁶ Yu et al. reported that SiO₂/C composites with 50.1% SiO₂ delivered a first discharge capacity of 536 mA h g⁻¹.⁷ Guo et al. fabricated SiO₂/hard carbon composites with a reversible capacity of 630 mA h g⁻¹, where SiO₂ yielded a reversible lithium storage capacity of 1675 mA h g⁻¹.⁸ Allcorn et al. developed crystalline FeSb₂ nanoparticles finely dispersed in an amorphous Al₂O₃ and carbon matrix through mechanochemical milling. The as-prepared electrode exhibited high stability (specific capacity = approximately 350 mA h g⁻¹ after 500 cycles) and fast high-rate (10 C) charge/discharge kinetics.⁹ However, depositing an even carbon coating on metal oxide surfaces is not possible at the molecular level. Moreover, metal oxide clusters are well covered by carbon layers, which crack easily during the early cycling stages because of capacity fading. Furthermore, these layers erode the solid electrolyte interface (SEI) during cycling. Thus, the low electronic conductivity of carbon (1.1 × 10⁻² S m⁻¹) is the primary challenge in its use as an electrode.

Among the Group 14 elements, Pb has high gravimetric capacity (582 mA h g⁻¹ vs. 372 mA h g⁻¹ of graphite), high volumetric capacity (6487 mA h cm⁻³), and a feasible working voltage (0.5–0.7 V) slightly above the lithium deposition potential. Currently, Pb is used in 86% of all U.S. automobile
lead-acid batteries.\textsuperscript{10} It is lower in cost and higher in availability and capacity compared with commercial graphite anodes,\textsuperscript{11} making lead-based compounds and composites high-potential LIB anodes. Many reports have been published on Pb-based anode materials, such as bare PbO,\textsuperscript{12,13} light-weight electrodes,\textsuperscript{14} P-doped lead oxides,\textsuperscript{15} and carbon composites.\textsuperscript{16,17} However, such anodes undergo at least a 40% volume change during alloying/dealloying, which pulverizes the active materials and causes low cyclability. Furthermore, the unstable SEI on Pb/PbO particles contributes to the low cyclability. Pulverization of active Pb particles was overcome by increasing the density of the loaded active and inactive materials; for example, Sn–Pb composite oxides exhibited a capacity of 550 mA h g\textsuperscript{-1} for 20 cycles;\textsuperscript{18} SiC–Pb–C composites yielded capacities exceeding 200 mA h g\textsuperscript{-1} for 200 cycles;\textsuperscript{19} and graphene-sandwiched PbTe nanoparticles exhibited a capacity of 500 mA h g\textsuperscript{-1}, which dropped to 300 mA h g\textsuperscript{-1} after 100 cycles.\textsuperscript{20} The microstructure of these electrodes are easily eroded over prolonged cycling. Another approach to controlling volume expansion during cycling is to increase the discharge cutoff voltage and limit the charge capacity; when this approach was applied, PbTe nanoparticles yielded a high capacity of 500 mA h g\textsuperscript{-1} for 100 cycles in the high potential region (0–2.5 V).\textsuperscript{21} The aforementioned techniques considerably enhance the cycling performance in half-cells but are ineffective in full-cell batteries with Pb-based anodes, primarily because of low capacity retention and unsatisfactory cycling stability caused by the low electronic conductivity and structural stability during charge/discharge, which influences LIB lifetime and electrode performance. For substantially improving the electrical contact and cyclability of lithium insertion reactions, Cu particles are preferred over metals such as Ag, Fe, Co, and Ni for forming the inactive matrix because of the high electrical conductivity of Cu (6 × 10\textsuperscript{6} S cm\textsuperscript{-1}).\textsuperscript{22} On lithiation, Cu atoms segregate on the Pb surface and maintain the electrical connection between the Pb particles. Moreover, Cu efficiently accommodates the structural strains associated with volume change and ensures contact between the active material and the electrolyte, thus facilitating charge transfer and lowering polarization. Therefore, we used Cu and C matrices with PbO active materials for forming stable nanostructure composites that accommodate volume changes and offer high conductivity, short lithium distances, and enhanced mass transport, which improve LIB structural stability and lifetime.

Among the many processes for uniformly distributing nanostructure composites, solvothermal synthesis is attractive because it affords precise control over size, shape distribution, and crystallinity and is highly adaptable to metal oxide nanoparticles and nanostructures.\textsuperscript{23} In this study, a new PbO/Cu–C composite was synthesized using solvothermal synthesis. To improve the electronic conductivity of the PbO electrode, Cu was introduced in the composite material through chemical reduction. C was used as the dispersive matrix for PbO because of its high conductivity and effective buffering of the active material volume change.\textsuperscript{24} Furthermore, polyvinyl pyrrolidone (PVP) dissolves in ethanol and water, thus facilitating obtaining a uniformly PVP-coated PbO precursor through precipitation. The performance of PbO/Cu–C composite materials was demonstrated in a complete battery test with LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} as the cathode material. The synthesized anode material exhibits excellent performance, as evidenced by its structural stability, high electronic conductivity, low discharge cutoff voltage, and high Li\textsuperscript{+} transport, and the proposed model has potential for flexible electronic applications.

2. Experimental section

Composites were prepared through solvothermal synthesis as follows: 1.5 mmol of cupric acetate (mol. weight: 181.63 mg, Acros Organics), 1 mmol of lead acetate (mol. weight: 325.29 mg of lead, Acros Organics), and 2 g of PVP (avg. weight 58 000 g mol\textsuperscript{-1}, Acros Organics) were mixed in 80 mL of pure ethanol, and the resulting solution was sonicated for 30 min. Next, a mixture of 5 mmol of NaBH\textsubscript{4} (Aldrich) in 20 mL of pure ethanol was added under sonication for 30 min, and the resulting solution was placed in an autoclave for 24 h at 180 °C. The PbO/Cu samples were washed through centrifugation several times. Subsequently, the samples were annealed in a vacuum furnace at 300 °C and 10\textsuperscript{-3} bar for 4 h to obtain PbO/Cu–C composites. The mass fraction of Cu loadings is approximately 83.75% (mCu/mPbO). For comparison, PbO–C composites were synthesized using the same procedures but without copper salt. Lead oxide (PbO) was purchased from Sigma Aldrich (particle size < 500 nm).

Because of a negative Gibbs free energy change (metal reactive series of Pb > Cu), the solvothermal process induces eqn (1).\textsuperscript{9} Under air and reducing agents, lead ions form lead oxide and copper without further oxidation (eqn (2)).

\begin{equation}
\text{Cu}^{2+} + \text{Pb}^{2+} \rightarrow \text{Cu}^{0} + \text{Pb}^{2+}
\end{equation}

\begin{equation}
\text{Cu}^{0} + \text{Pb}^{2+} \xrightarrow{\text{Air}} \text{Cu}^{0} + \text{PbO}
\end{equation}

The Fourier-transform infrared (FTIR) spectra of samples were recorded using a Perkin Elmer Spectrum 500 spectrometer in the 4000–450 cm\textsuperscript{-1} range by using the KBr pellet method. X-ray diffraction (XRD) patterns were measured using a Bruker D8 Tools Advance diffractometer operated with Cu Kz radiation ($\lambda = 1.5406 $ Å) at 40 keV and 40 mA. Sample morphology and microstructure were characterized using scanning electron microscopy (SEM; JSM-6500F, JEOL) and transmission electron microscopy (TEM; G2 FEI-TEM, Philips Technai).

Electrochemical properties were investigated using CR-2032 coin cells. A 0.3 mm-thick metallic lithium foil (UBIQ Tech. Co. Ltd) and the PbO/Cu composite were used as the counter and working electrodes, respectively. The working electrode was prepared by casting a slurry containing an active material, super P, and polyacrylic acid (Aldrich, avg. weight 1800 g mol\textsuperscript{-1}) on a copper foil at a 60 : 20 : 20 weight ratio in ethanol and drying the electrode in a vacuum oven at 80 °C for 12 h. The mass loading of active material on each anode was approximately 0.1–0.3 mg and the electrode thickness was approximately 4.5 μm. Both electrodes were electronically separated using a Celgard 2600 (25 μm thickness, 28 nm pore size, UBIQ Tech.) as the
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3. Results and discussion

To investigate the chemical and structural nature of the synthesized PbO/Cu–C, PbO/Cu, and PbO–C samples and the effects of the chemicals used in their synthesis, FTIR analysis was conducted (Fig. S1 (ESI†)). The characteristic bands at 480 and 848 cm$^{-1}$ observed for PbO in different samples are attributable to Pb–O vibrations. The shoulder band at 1416 cm$^{-1}$ is due to the vibrations of strong O–Pb bonding in different samples. The peaks around 2347 and 3427 cm$^{-1}$ correspond to bending vibrations of the absorbed molecular water and stretching vibrations of –OH groups in all samples. The samples did not exhibit the N–PbO (JCPDS no. 85-1287, 2000), β-PbO (JCPDS no. 76-1796, 200), a small quantity of 2PbO–PbO$_2$ particles, and copper (JCPDS no. 04-0836). No specific peaks were observed for the carbon matrix. In addition, the intense and sharp diffraction peaks suggest that the obtained products were well-crystallized composites. The average crystal size, calculated using the Debye–Scherrer formula with crystalline Si as the reference material, decreased from approximately 30 to <10 nm (Cu and PbO particles) after heat treatment.

SEM images of PbO/Cu and PbO/Cu–C composites are depicted in Fig. 1A and B. The PbO/Cu–C images reveal that the particles remain well-defined agglomerates with distinct inter-spaces, whereas particles in the PbO/Cu composite vary in size from <100 to approximately 20 nm. During the high-temperature treatment, the composite particles, assisted by PVP, increasingly agglomerated and segregated, creating inter-spaces; such interfaces likely facilitate buffering to accommodate the cyclic volume change of the electrodes. Furthermore, as shown in Fig. 1C and D, the fabricated PbO/Cu–C composite electrode displays uniform coating on the copper foil, which even after 5000 cycles at 5.5 A g$^{-1}$ did not crack or break. Similarly, the TEM image of the PbO/Cu–C composite showed distinct but unevenly distributed inter-space particles with a size of approximately 20 nm, which is smaller than that of PbO/Cu particles. The decomposition of PVP to carbon in the composites is depicted in Fig. 2A and B. The high-resolution TEM (HRTEM) images of as-synthesized PbO/Cu and PbO/Cu–C composites depicted in Fig. 2C and D reveal that the PbO/Cu–C composite particles agglomerate more. The copper and lead oxide particles are intermixed and surrounded by the amorphous carbon matrix, which offers effective mechanical reinforcement, accommodates the volume change of the PbO particles, and separates and inhibits PbO agglomeration during prolonged cycling. The SEM images of the prepared (A) PbO/Cu composite, (B) PbO/Cu–C composite, and PbO/Cu–C composite fabricated with binder on copper (C) before and (D) after 5000 cycles.
Impedance spectra provide further information on anode performance. Nyquist plots of various electrodes are presented in Fig. 3C; the plots are semicircular in the high-frequency region and straight at lower frequencies, indicating the charge-transfer resistance and charging capacitance and the Warburg diffusion impedance, respectively.\textsuperscript{39,41} These semicircles indicate the formation of SEIs caused by the decomposition of the electrolyte, and the sloping straight line corresponds to Li-ion diffusion in the bulk electrode.\textsuperscript{40} The fabricated PbO/Cu–C composite electrode exhibits low charge-transfer resistance, which suggests improved kinetic transport for electrode reactions with strong electrical contact and high charge-transfer resistance. Furthermore, the CV curves of the PbO/Cu–C composite electrode after different cycles (Fig. 3D) reveal that impedance changes during the first few cycles slow the wetting of the electrolyte and that the conductivity increases after Li-ion doping during charging.\textsuperscript{3} The second semicircle in the medium-frequency regions corresponds to the electrochemical alloying of Li with PbO/Cu–C. Film passivation occurs during lithiation, and delithiation of the PbO/Cu–C composites is accompanied by Li-ion diffusion through the SEI and blocking electrode (eqn (3)).\textsuperscript{42,43} Prolonged cycling does not considerably change the impedance spectra, indicating the limited progress of SEI during cycling (Fig. S5†). After 9500 cycles, the electrode loses capacity completely because of electrolyte decomposition and overheating caused by active material degradation.\textsuperscript{44,45}

Galvanostatic charge/discharge studies were used for evaluating the anode materials in the 0.05–1.2 V (vs. Li+/Li) voltage range. PbO–C and commercial PbO materials are compared in Fig. 4A, which depicts their performance in several selected cycles at a current density of 1.0 A g$^{-1}$. The PbO/Cu–C electrode exhibits a relatively stable reversible capacity of 320 mA h g$^{-1}$ in 4000 deep cycles based on the weight of the active material (not shown in figure). In comparison, the PbO–C composite electrode loses approximately 25% of its first-cycle capacity, and commercial PbO yields a capacity of 128 mA h g$^{-1}$ after 100 cycles. Moreover, the Coulombic efficiencies (CEs, delithiation capacity/lithiation capacity) of PbO/Cu–C and PbO–C clearly shows the irreversible reactions during first discharge, with multiple reduction peaks for the conversion of PbO to Pb and the formation of Li$_2$O; in addition, some intermediates are formed (Pb') during the Pb$^{2+}$ to Pb$^0$ reduction.\textsuperscript{37,38} Electrolyte decomposition and stable SEI formation occur at 0.7 V (eqn (3)) in the first but not in subsequent cycles.\textsuperscript{44,45} In subsequent scans, two pairs of redox peaks appear at 0.2–0.65 V, corresponding to the formation of $0 < y < 4.5$ (LiPb, Li$_2$Pb, Li$_{1.5}$Pb, and Li$_4$Pb alloys; eqn (4) and (5)).\textsuperscript{13} Additionally, after the first cycle, the peak currents and areas do not change in the wide potential range between 0.005 and 1.0 V, indicating the electrode stability and excellent charge/discharge profile of the composites. Fig. 3B shows a comparison of the electrochemical behaviors of the PbO/Cu–C composite with those of PbO–C and commercial PbO composite electrodes. The current densities and redox peaks of the PbO–C and commercial PbO electrodes are lower than those of the PbO/Cu–C composite electrode, indicating its excellent reversibility and structural stability during cycling. According to the CV curves, the reaction mechanism in the first cycle is

\begin{align}
\text{Li}^+ + e^- + \text{electrolyte} & \rightarrow \text{SEI(Li)} \\
PbO_x + 2\text{Li}^+ + 2e^- & \rightarrow Pb + x\text{Li}_2O \\
Pb + y\text{Li}^+ + xe^- & \leftrightarrow \text{PbLi}_y
\end{align}

Fig. 2 TEM images of (A) PbO/Cu composite and (B) PbO/Cu–C composite (buffer layers: copper and carbon); (C) HRTEM images of PbO/Cu composite and (D) PbO/Cu–C composite (inset: corresponding SAED patterns).
composites in various cycles are plotted in Fig. S6;† the trend is consistent with those of cycle life and capacity. In the first cycle, the PbO/Cu–C composite exhibits a CE of 54.4%, which is attributable to irreversible loss because of SEI and Li₂O formation,¹⁶–¹⁸,⁴¹–⁴³ whereas the CE is >99.6% throughout the 100 cycles, this is attributed to: (a) the reversible conversion of Pb after discharge to lithiated PbO after charge, (b) Cu and C acting as the buffering media that accommodates the stress induced during lithium insertion and extraction, and (c) Cu acting as not only the buffering media but also the conducting media for electronic conduction between PbO particles, thus maintaining consistent a CE.²² According to the CE, we conclude that stress is induced only during the first cycle. However, the stress induced in the first cycle was not calculated in this study (the detailed stress calculation will be presented in our upcoming study). PbO–C composites initially exhibit a CE of approximately 34%; the CE rapidly increases over 20 cycles and becomes as high as 97% between cycles 20 and 100. For PbO/Cu–C, the CE is consistently between 98% and 99.6%. The initial CE and first-cycle lithiation capacity loss of the synthesized electrode and other carbon-based composites are compared in Table 1.⁴⁶–⁵⁴ The synthesized electrode is superior to the other carbon-based composite electrodes. The voltage profile of the composite electrode at different cycles is illustrated in Fig. 4B. The plateaus of the voltage profiles are consistent with their corresponding CV peaks. The first discharge (alloying) and charge (dealloying) capacities of the fabricated system are 710 and 336 mA h g⁻¹, respectively; the loss is due to electrolyte decomposition and SEI formation on the electrode surface and surface PbO reduction.⁴¹–⁴³ After the first cycle, the electrode was stable, affirming the

Table 1 Calculated first-lithiation capacity, first-lithiation capacity loss (first lithiation capacity – second lithiation capacity)/first lithiation capacity]) and Coulombic efficiency (CE) of carbon-based composite anodes

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<th>Electrodes</th>
<th>1st Lithiation capacity/mA h g⁻¹</th>
<th>1st Cycle lithiation capacity loss/mA h g⁻¹</th>
<th>1st CE/%</th>
<th>Rate/mA g⁻¹</th>
<th>Ref.</th>
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<tr>
<td>PDPC/WS₂</td>
<td>625</td>
<td>50.8</td>
<td>49.1</td>
<td>200</td>
<td>46</td>
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<td>CB-GeO₂/C</td>
<td>2220</td>
<td>49.0</td>
<td>50.2</td>
<td>550</td>
<td>47</td>
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<td>Sn-CNFs</td>
<td>2716</td>
<td>57.0</td>
<td>43.0</td>
<td>100</td>
<td>48</td>
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<td>AgNPs/TiO₂/C</td>
<td>1323</td>
<td>58.0</td>
<td>41.1</td>
<td>100</td>
<td>49</td>
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<td>MoS₂-RGO</td>
<td>590</td>
<td>130.0</td>
<td>51.2</td>
<td>100</td>
<td>50</td>
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<tr>
<td>Sn₀.₉₂Sb₀.₀₈@C/CNFs</td>
<td>1070</td>
<td>47.0</td>
<td>52.1</td>
<td>50</td>
<td>51</td>
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<tr>
<td>Fe₇₋₆Fe₆₋₅/CNFs</td>
<td>961</td>
<td>45.0</td>
<td>52.1</td>
<td>200</td>
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<td>SnO₂NWs-C</td>
<td>1983</td>
<td>67.0</td>
<td>32.8</td>
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<td>N-OMC/SiO₂</td>
<td>3900</td>
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<td>PbO/Cu–C</td>
<td>710</td>
<td>52.0</td>
<td>54.4</td>
<td>1000</td>
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electrochemical reversibility of the material. Furthermore, CuO formation on PbO/Cu–C is limited because of its negligible weight and high capacity. Moreover, peaks corresponding to CuO were not observed in the CV, XRD, and FTIR measurements of the composite electrode. The capacity of the PbO–C composite electrode was high for some cycles but subsequently rapidly decreased; commercial PbO electrodes have weak capacity and stability (Fig. 4A). The PbO/Cu–C composite electrode exhibits enhanced performance because Cu and C are employed as the conductive material and dispersive matrix, respectively.25,26 Thus, the capacity of PbO/Cu–C composites is higher and more stable than that of PbO–C composites.

The rate performance of the PbO/Cu–C composite electrode plotted in Fig. 4C reveals the variation of current density (0.165, 0.275, 0.385, 0.55, 1.0, 2.75, 5.5, and 0.165 A g\(^{-1}\)) with capacity (420, 370, 340, 310, 206, 160, 86, and 390 mA h g\(^{-1}\), respectively). The current density is suppressed to 0.165 A g\(^{-1}\) and the capacity is recovered (retention rate >90%). Even at high currents, the lithiation potential is identical to that at low currents. Clearly, lithium rapidly penetrates the conductive and buffer layers and contacts PbO material in all electrodes.

A long-term deep cycling test was conducted using fast charge/discharge currents. As shown in Fig. 4D, the electrode capacity of 72 mA h g\(^{-1}\) at a current density of 5.5 A g\(^{-1}\) was retained, with slight changes, in up to 9500 cycles with a CE of approximately 99.8%, which indicates the superior and stable cycling performance of the fabricated electrode. The high CE is due to Cu and C acting as buffering media that accommodate the stress induced during lithium insertion and extraction; furthermore, Cu facilitates electronic conduction between the PbO particles.27,28

Finally, to demonstrate the practical application of the as-synthesized PbO/Cu–C composite in LIBs, we investigated the performance of a CR2032 coin-type full-cell device with the PbO/Cu–C composite as the anode and LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) as the cathode. The cathode was fabricated as reported earlier29 and is detailed in ESI section 1.† The theoretical reversible capacity of the cathode is approximately 274 mA h g\(^{-1}\) in the 2.4–4.6 V range.25 A voltage window of 2.4–4.4 V was used in the experiment, with lithium foil as the counter electrode (Fig. S7†). The practical reversible capacity of the LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) cathode is approximately 172 mA h g\(^{-1}\). Cyclic voltammograms of the full cells (LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) vs. PbO/Cu–C composite, voltage window of 0.05–4.8 V at a scan rate of 0.1 mV s\(^{-1}\)) are shown in Fig. S8†. The potential peak assignments are 3.7–3.9 V (Ni\(^{2+}/Ni^{3+}\)), 3.9–4.4 V (Ni\(^{3+}/Ni^{4+}\)), and 4.4–4.6 V (Co\(^{3+}/Co^{2+}\)). The Mn\(^{4+}\) ions in the cathode oxide cannot participate in the redox processes between 2.5 and 4.7 V.30 The voltage profile of the full cells recorded at 100 mA g\(^{-1}\) in the window 0.05–4.8 V is presented in Fig. 5A. During charge, lithium is extracted from the LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) cathode and transferred to the PbO/Cu–C composite anode; during discharge, the process is reversed through electrolysis. The first-charge capacity is approximately 190 mA h g\(^{-1}\), lower than that of lithium in the cathode, and the discharge capacity is 109 mA h g\(^{-1}\), because of the irreversible anode reaction. The capacity gradually decreases with cycling.

Fig. 5 demonstrates the cyclic performance and Coulombic efficiency of the as-developed device. The first-charge Coulombic efficiency is 68.8%, which is appropriate for practical applications. The capacity gradually decreases up to 34 cycles, after which a stable reversible capacity of 178 μA h and Coulombic efficiency of 97% are achieved. Additional studies (charge/discharge process and cathode/anode balance) are necessary for realizing stable performance at higher Coulombic efficiencies.

4. Conclusion

Nanostructured PbO/Cu–C composites synthesized through in situ solvothermal synthesis exhibited a high stability of over 9500 cycles and capacity retention of approximately 98% from the second cycle at a high current density of 5.5 A g\(^{-1}\). The composite exhibits reversible charge–discharge processes at a high Coulombic efficiency exceeding 99.6%. Such stable properties of PbO/Cu–C are attributed to the relatively small volume change of the active PbO particles during cycling, the buffering effect of the inert matrix on volume expansion, and the improved electronic conductivity of the fabricated electrode. The electrode can be effectively used as an anode in full cells with LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) as the cathode, as experimentally demonstrated in this study. Furthermore, works are in progress for extending this design approach to other materials such as silicon and tin.

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