

Preparation of Graphene Shell and Its Applications in Lithium-ion Batteries

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Introduction

Graphene has large specific surface area, good electrical and thermal properties, which is an ideal anode nanomaterial for lithium ion batteries. In this project, a multilayer graphene shell (Gr-S), which morphology & layer numbers can be controlled by hours, structured by CVD method. Microscopy technology revealed the correlation between its structure and specific capacity during charge-discharge performance. The lithium storage mechanism of graphene shells was explored.

Experimental Section

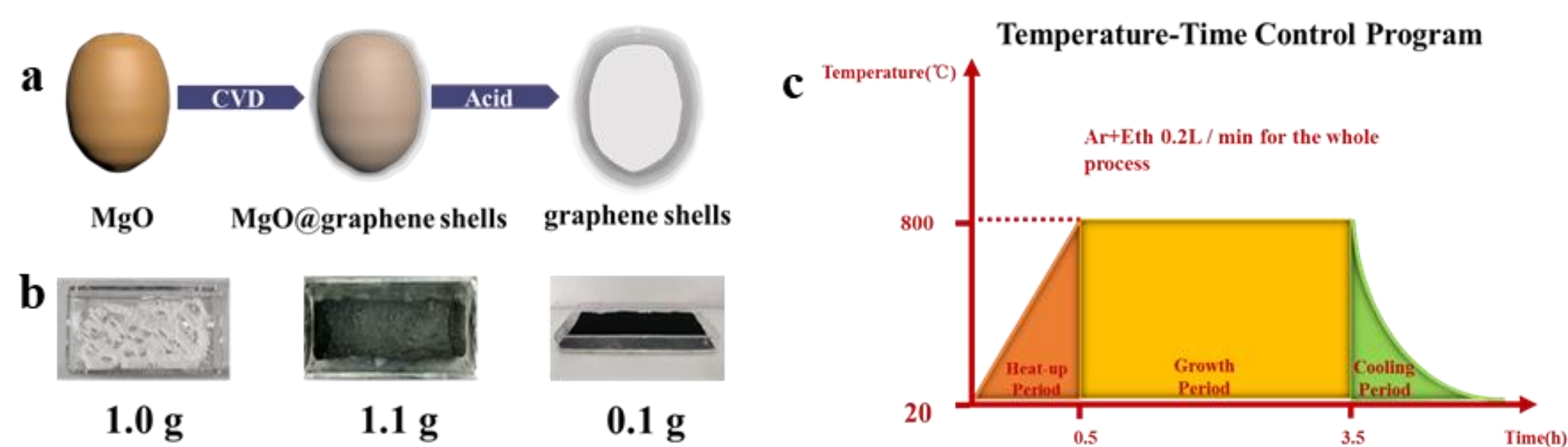


Figure 1. (a) Scheme for preparation of graphene shells use CVD method. (b) A schematic illustration for the formation process of the graphene shells. (c) Graph of temperature-time control program for the formation of the graphene shells.

4.0 g nanostructured MgO with diameter of about 50 nm is evenly put on the quartz boat, followed by heating treatment in atmosphere of Ar at a flow rate of 200 mL/min for 1h, 2h, 3h, 4h and 6h respectively. The reactions are constructed at a temperature of 800 °C, followed by cooling down to room temperature under the Ar flow. The graphene shells (GSs) are finally obtained by acid treatment in 1 M/L HCl.

Results and Discussions

Morphology Characterization

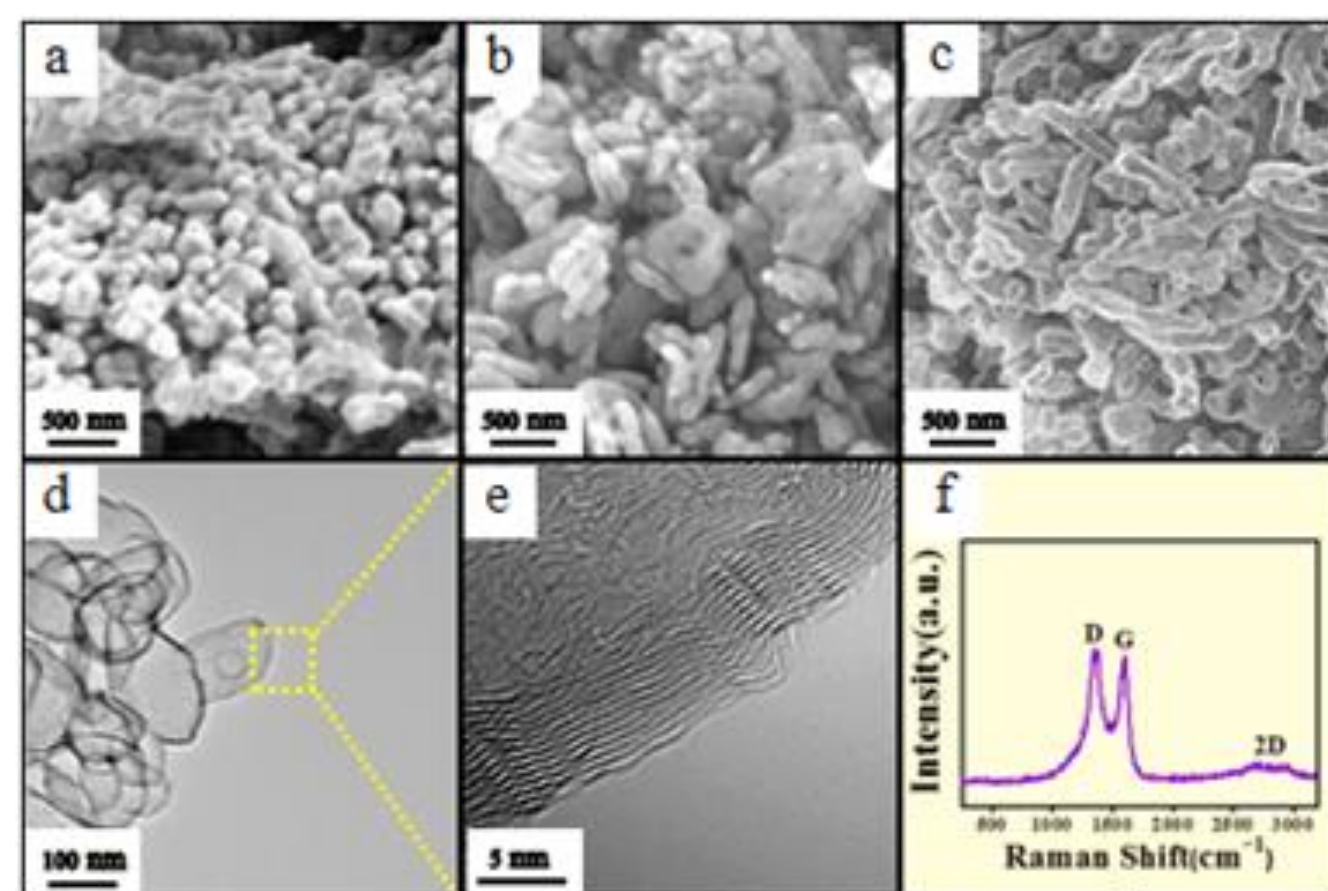


Figure 2. SEM images of (a) MgO; (b) MgO@GS 3h; (c) GS 3h. (d) TEM image of GS 3h; (e) HR-TEM image of GS 3h; (f) Raman spectrum of GS 3h.

SEM and TEM image reveal clearly the structural characteristics of the GSs, which display distinct hollow structure with multilayers (Figure 2 a-e). Raman spectrum investigates the high graphitization degree of GSs.

Mathematical statistical analysis of layer numbers of Graphene Shells shows that the number of layers grows up gradually with reaction time, while the increasing trend slows down after 3 hours (Figure 3d). Within a long enough time, nanoparticles have been adhered with each other into sheets and start overlapping to form bulks by then. Thus, by adjusting the reaction time during the chemical vapor deposition, the layer number of graphene shells can be controlled.

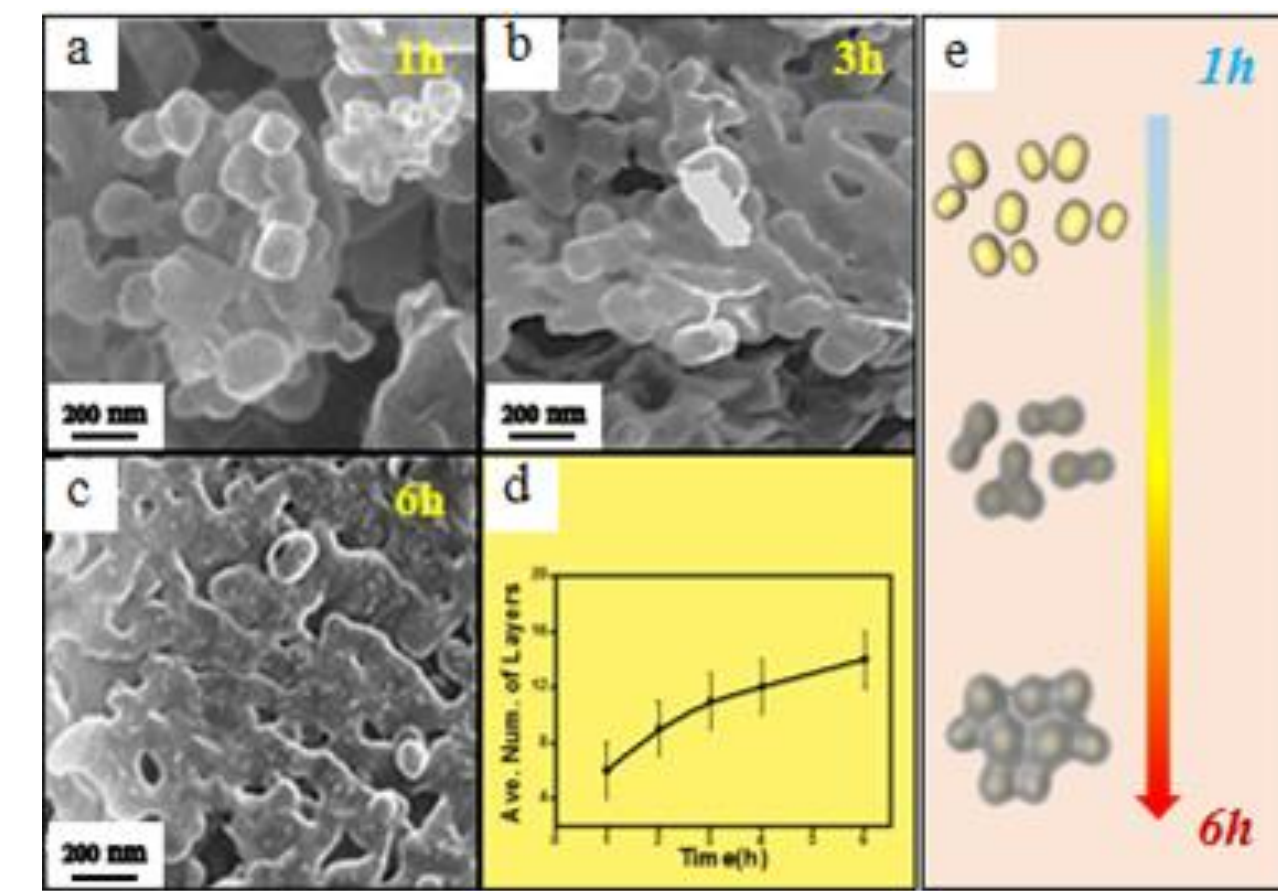


Figure 3. (a-c) SEM images of MgO@GS for different CVD reaction hours. (d) Average number of layers under different reaction hours. (e) Scheme of growth behavior with the increase of time.

Graphene shells of different hours all have a high level of graphitization (figure 4a). With increase of the reaction time, the ratio of ID/IG gradually increased, indicating that the degree of graphitization of GSs increased and defects decreased meanwhile. The BET results show that from one hour to six hour, GS's pore diameter increases and the specific surface area decreases.

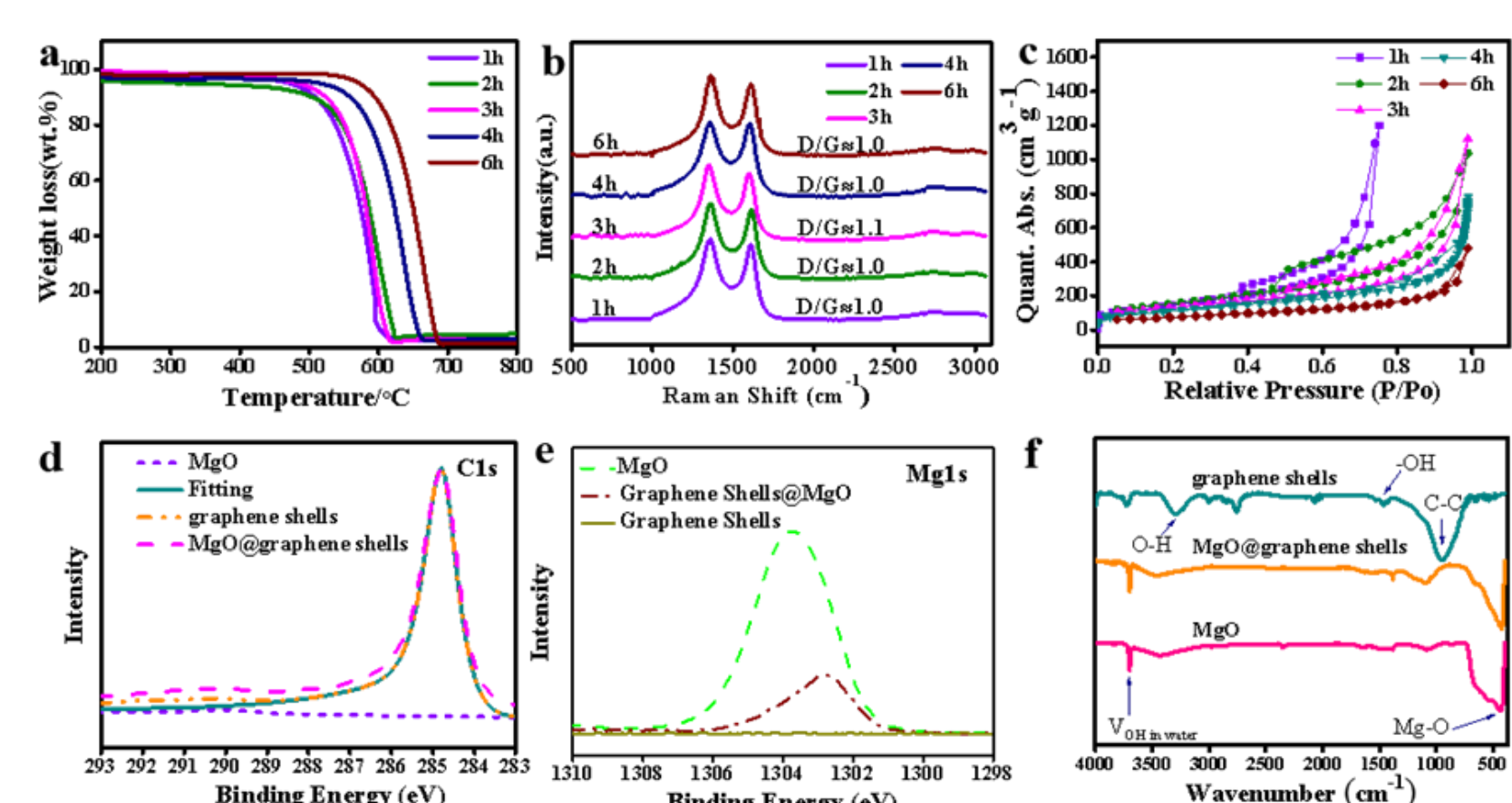


Figure 4. Thermal analysis, Raman and N₂ adsorption-desorption characterizations on the GS(1h, 2h, 3h, 4h, 6h). (a) Thermogravimetric curves. (b) Raman spectrum. (c) N₂ adsorption and desorption isotherms. XPS analysis and FTIR analysis of MgO, MgO@GS(3h) and GS 3h. (d) C 1s; (e) Mg 1s; (f) FTIR.

Conclusions

We have developed an easy strategy for the fabrication of graphene shells. According to the batteries tests, graphene shells exhibit excellent electrochemical performance as anode materials of lithium ion batteries, including an outstanding large specific capacity (almost three times that of graphite), better rate performance (have a capacity of almost 250 mAh/g even after 1000 cycles at the current density of 21600mA/g). Additionally, we also focused on the modification of the GSs and optimization of battery craft (electrolytes, separator, binders and so on). Take the consideration of the limited space, the data for this part is omitted.

Electrochemical Performance

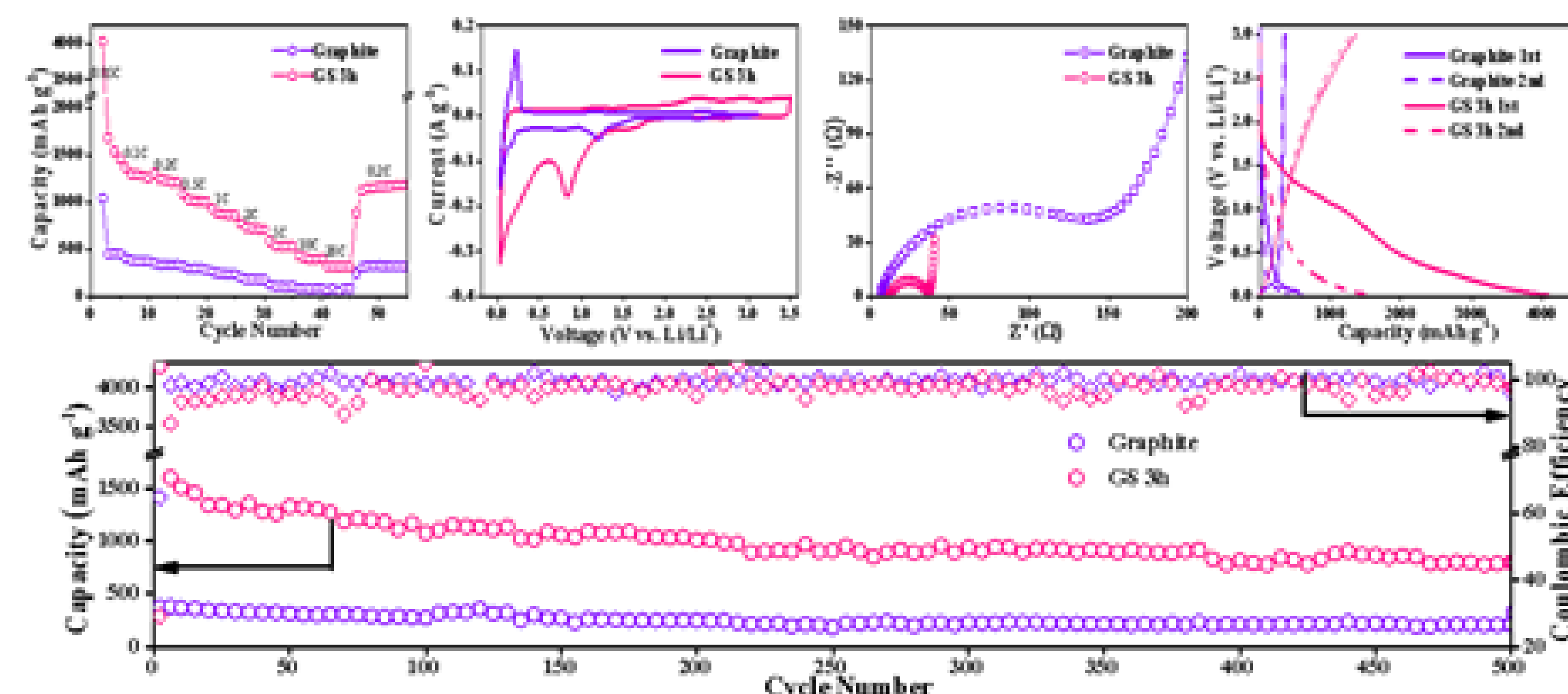


Figure 5. Electrochemical performance of Graphene shells and Graphite electrode. (a) Rate performance at different current densities (from 0.05C to 30C). (b) CV at a scan rate of 0.1 mV s⁻¹. (c) EIS. (d) Galvanostatic charge/discharge voltage profiles of Graphite and GS measured at 0.1 C. (e) Cycling performance and Coulombic efficiency at 0.1 C.

The electrochemical properties of GSs as anode material in Lithium-ion batteries have been evaluated by charge-discharge measurement, electrochemical impedance spectroscopy and cyclic voltammetry.

Electrochemical tests show that, compared to graphite, GS has a superior electrochemical performance as anode material, including an outstanding larger specific capacity (almost three times of commercial graphite), better rate performance and lower impedance values.

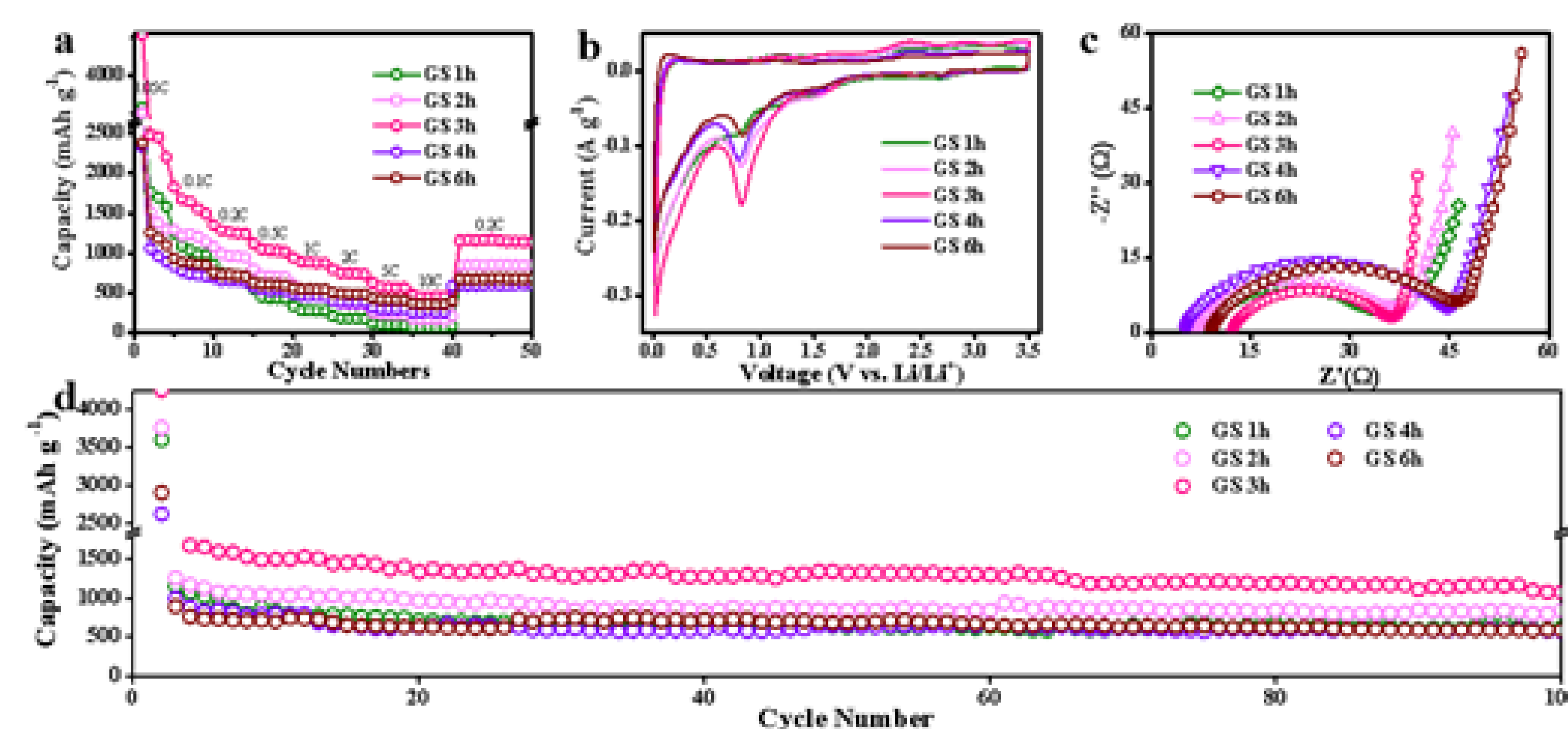


Figure 6. Electrochemical performance of GS of different hours (a) Rate. (b) CV curves. (c) EIS. (d) Long-term cycling at a current density of 0.1C.

Graphene Shell prepared at 800°C with 3h has an optimal electrochemical performance (Figure 5): better continuity and consistency at rate tests; a high and stable discharge specific capacity during cycling.

As growing hour increases, layer number of a single graphene shell increases, resulting in the specific capacity of graphene shells show a bell-curve mode at a constant current density.

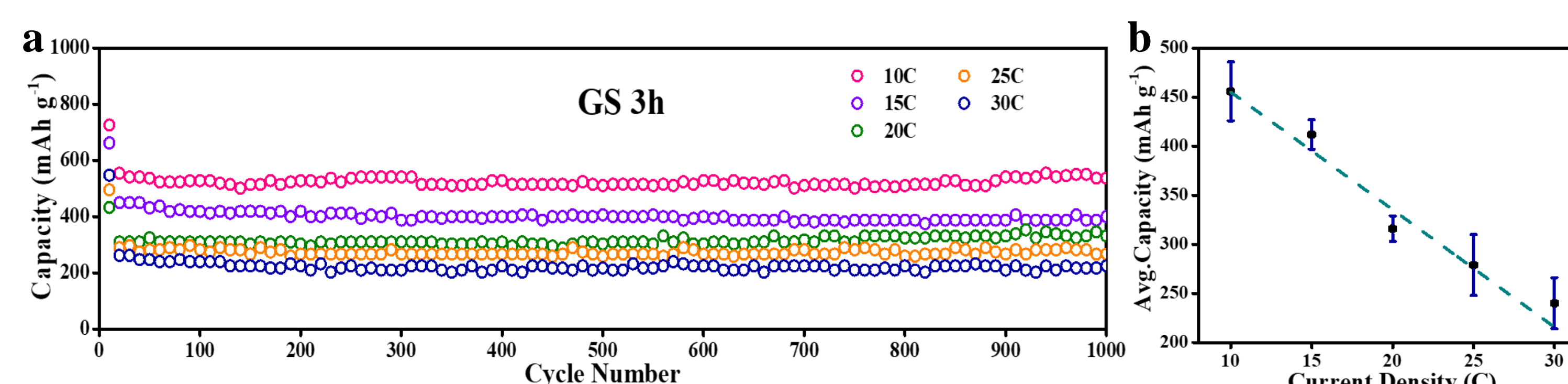


Figure 7. (a) Cycling performance corresponding voltage profiles of GS 3h at a current density of 10 C, 15 C, 20 C, 25 C, 30 C; (b) Average number of specific capacity of GS 3h at different current density.

Good performance of GS at high current density is shown in Figure 7, which shows that they have a reversible capacity of 510 mAh/g, 400 mAh/g, 340 mAh/g, 270 mAh/g and 210 mAh/g without noticeable fading up to 1000 cycles at high current density of 7200mA/g, 10800mA/g, 14400mA/g, 18000mA/g, 21600mA/g respectively.