

Supplementary Information

Significant differences in the electrochemical activity of black phosphorus anodes prepared under different atmospheres

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Experimental Section

Sample Preparation: The bulk black phosphorus (BP) crystals were provided by Shangdong Yueneng New Materials Science and Technology Co., Ltd. The large BP crystals were first processed by ball milling. The ZrO₂ balls of 5 mm and 3 mm diameter were mixed (mass ratio: 2:1) for the ball milling process. Typically, an 80 ml milling jar was filled with 1 g of BP and 15 g of ZrO₂ balls in an Ar-filled glove box, and the milling jar was sealed before being taken out of the glove box. The bulky BP was then transferred to a planetary ball-milling machine (Retsch, PM 200) and ball-milled for 40 h at the speed of 300 rpm to produce the BP powder. BP/Li half-cells were assembled and after 1 cycle the BP/Li cells were disassembled in a glove box to obtain BP-Air and BP-Ar anodes. The charged BP-Air and BP-Ar anodes were washed three times with dimethyl carbonate (DMC) to remove residual electrolytes and dried in a vacuum chamber before further analysis.

Electrochemical Measurements: The battery charging tests for BP/Li half-cells were carried out using a Land CT2001A battery test system (Wuhan, PR China) in a voltage range of 0.01–2.0 V at room temperature. The cells were discharged at 0.05 C to 0.01V and the charge at 0.05 C to 2 V. Electrochemical impedance spectroscopy (EIS) measurements was carried out on an electrochemical workstation (Autolab, Metrohm) in a frequency range of 100 kHz to 10 mHz with a voltage amplitude of 5 mV.

Half-Cell Assembly: The BP/Li half-cells were assembled using CR2032 coin cell modules in an argon-filled glove box. The BP powder was mixed with Carbon ECP and poly-vinylidene (PVDF) solution (dissolved in NMP) in air and argon respectively were mixed by a weight ratio of 7:2:1 to make the electrode slurry and then were coated on a copper current collector. The prepared BP-Air anodes were pre-dried in a DHG-9035A air blast drying oven (Yiheng Scientific, Shanghai, China) at 55°C for 20 hours for the removal of NMP solvent. Meanwhile, the prepared BP-Ar anodes were directly placed in the antechamber vacuum oven of the glove box (MBRAUN, UNIlab Pro) for pre-drying at 55 °C for 20 hours. Afterwards, the as-prepared BP-Air and BP-Ar electrodes were punched into small disks (Φ 12 mm), with active mass loadings of 1.55 mg/cm² and 1.38 mg/cm², respectively. To remove any traces of water, the BP-Air and BP-Ar anodes were further dried in vacuum at 120 °C for 6 hours by using a DZF-6096 vacuum oven (Yiheng Scientific, Shanghai, China) and an antechamber vacuum oven of the glove box (MBRAUN, UNIlab Pro), respectively. In addition, some of BP-anodes were vacuum-dried at various temperatures to investigate the effect of temperature during the electrode drying procedure. The as-prepared electrode sheets Lithium foil was used as both the counter electrode and reference electrode. The electrolyte was typically 1 m LiPF₆ in ethylene (EC) and dimethyl carbonate

(DMC) (1:1 in volume, without additives) and the separator was Al₂O₃ coated polyethylene (PE) film.

Characterizations: The morphologies of pristine and cycle BP-Air and BP-Ar anodes were characterized by scanning electron microscopy (SEM, S-8100, Hitachi). The elemental composition and valence states of the surface of pristine and cycle BP-Air and BP-Ar anodes were obtained using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific). The XRD measurements were conducted in a Bruker D8 Advance diffractometer Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) in the 2θ scan range of 10-80°. The elemental content of powder scraped from BP-Air and BP-Ar anodes were determined by inductively coupled plasma (ICP) analysis using an Agilent 5110 ICP-OES instrument.

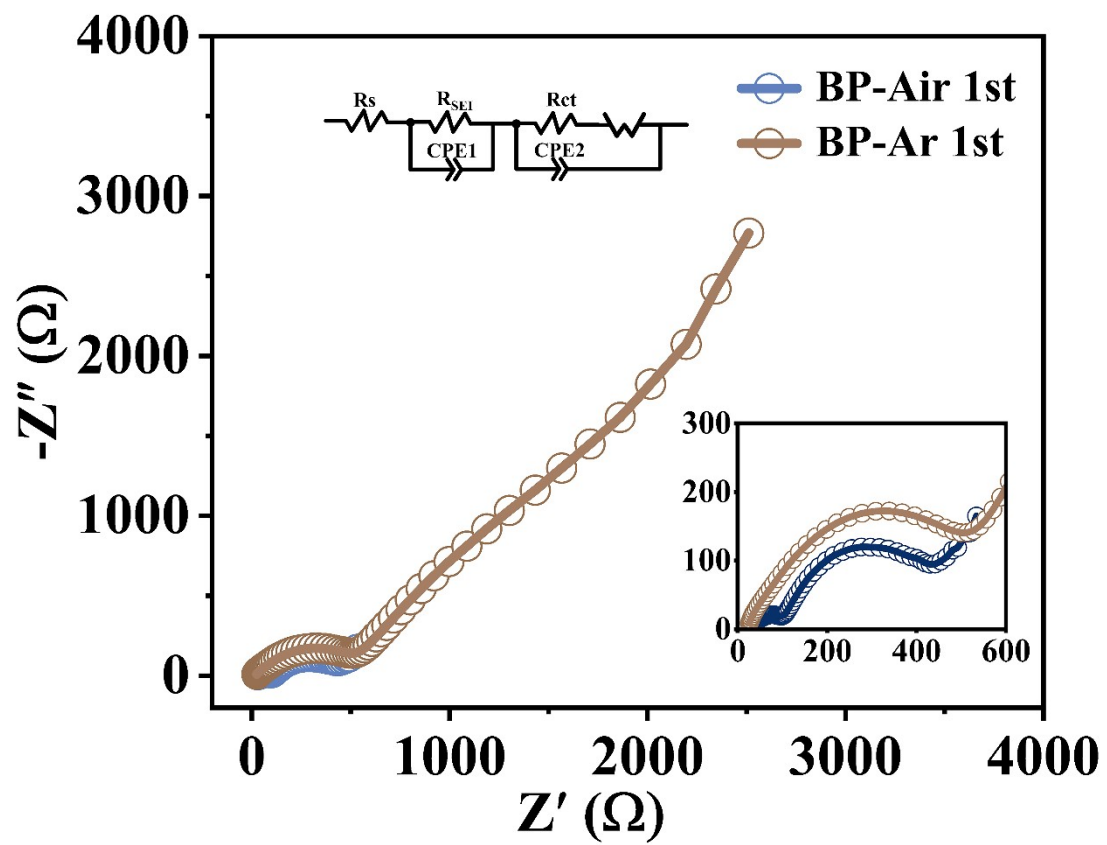


Figure S1. EIS curves of BP-Air and BP-Ar after 1 cycle.

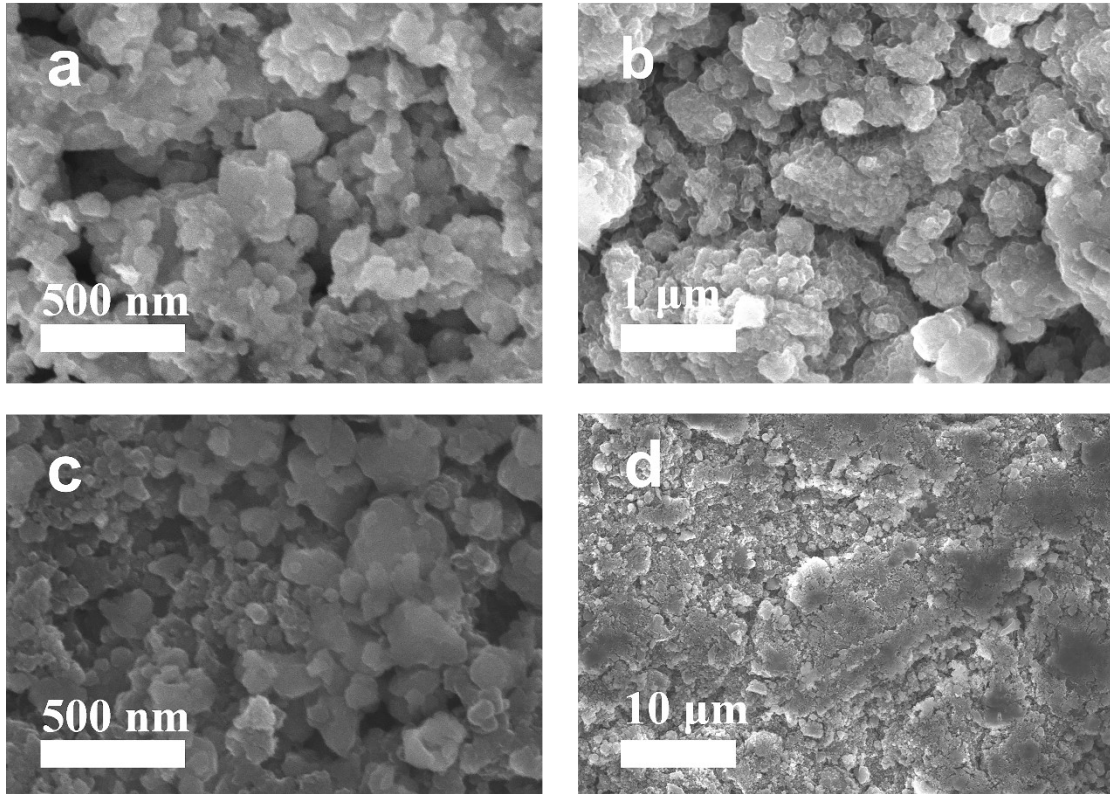


Figure S2. The SEM (a and c) of the BP-Air and the BP-Ar Pristine anode, the SEM (b and d) of the BP-Air and the BP-Ar anode after 1 cycle.

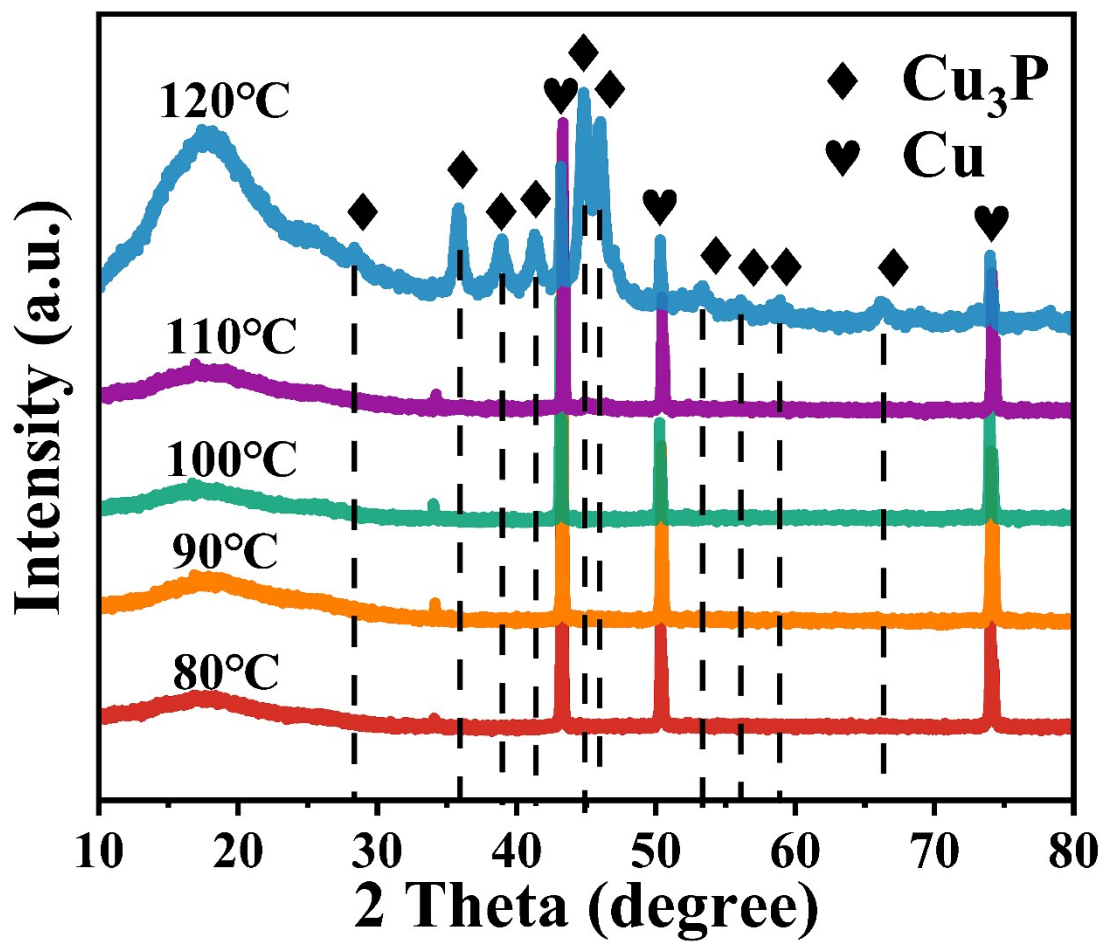


Figure S3. The XRD pattern of the BP-Air anode at different vacuum drying temperatures.

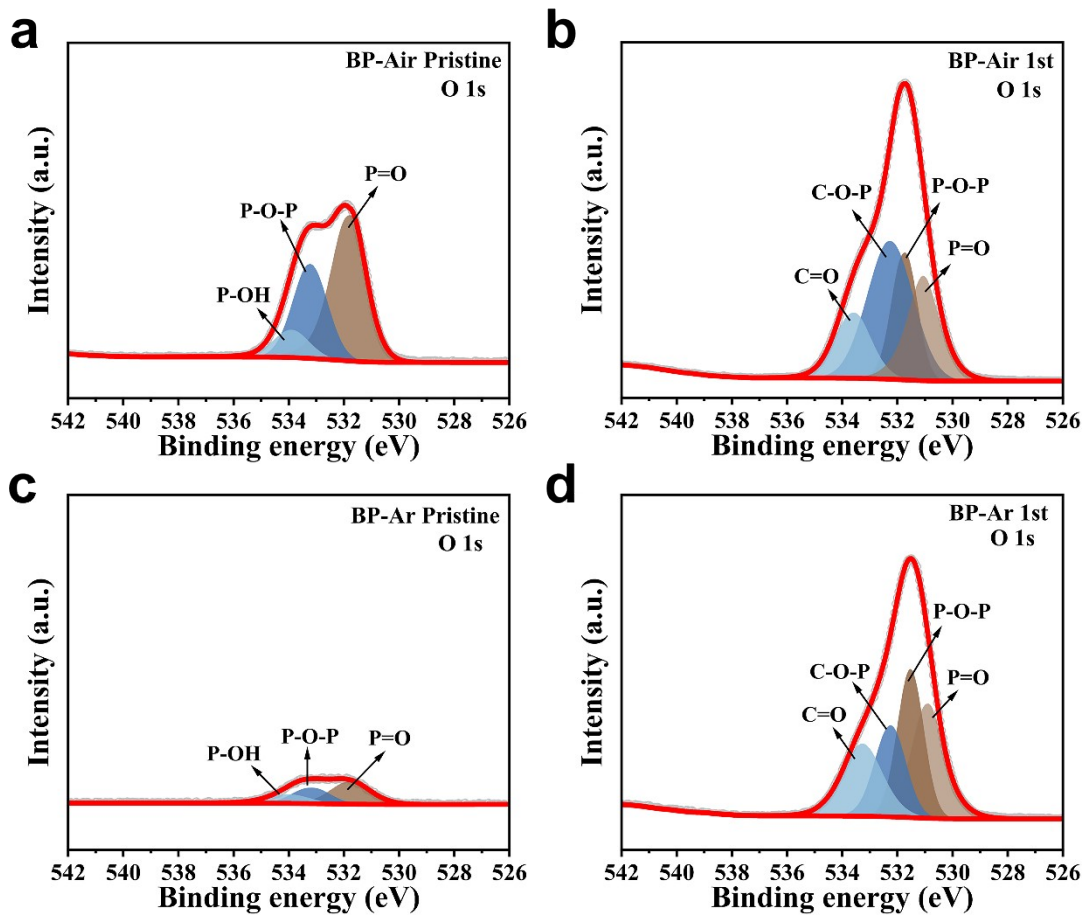


Figure S4. The O 1s spectra of pristine and cycled (a, b) BP-Air and (c, d) BP-Ar anodes

Sample	Cu (ppm)	P (ppm)	%RSD
Powder (BP-Air)	5.97	1.84	0.77
Powder (BP-Ar)	0.09	7.91	1.67

Table S1. ICP-OES test results of powder scraped from the BP-Air and BP-Ar electrodes