Supporting Information

Synthesis of Porous Carbon Supported Palladium Nanoparticle Catalysts by Atomic Layer Deposition: Application for Rechargeable Lithium-O₂ Battery

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Supplementary Figure S1

Fig. S1 (a) SEM image of 10c Pd-ALD coated carbon; (b) EDX elemental mappings of C; and (c) EDX elemental mapping of Pd.

Supplementary Figure S2

Fig. S2. SEM images of SPL carbon before (a) and after (b) being loaded with Pd nanoparticles ALD approach.

Supplementary Figure S3

Fig. S3. SEM image of the 3c-ALD Pd/C cathode harvested after 1st discharge

Supplementary Figure S4

Fig. S4. SEM image of the bare carbon cathode harvested after 1st discharge

Supplementary Figure S5

Fig. S5. SEM image of the 3c-ALD Pd/C cathode harvested after 1st charge

Experimental section

1 Preparation and Electrochemical Evaluation of ALD Pd/C Cathodes

Super P[®] Li conductive carbon black with a typical particle size 40 nm and a surface area 62 m²/g was used as the catalyst support material. Prior to the Pd ALD, Super P Li carbon was treated using a KMnO₄ solution (1 mol/L). This oxidizing agent partially oxidizes the carbon surface and forms oxygen-containing functional groups. These acidic groups improve the catalytic and adsorptive properties of the carbon materials. Moreover, the oxidation introduces surface hydroxyl groups that facilitate the chemisorption of the ALD Pd precursor.^{1,2}

ALD was performed in a continuous-flow stainless steel reactor described in detail elsewhere³. About 100 mg of the Super P[®] Li carbon powder was carefully spread onto a stainless steel tray, and a stainless steel mesh cover was clamped over the tray to contain the powder while still providing access to the ALD precursor vapors. The carbon powder was held in the reactor at 200 °C under continuous flow of 300 sccm ultra-high-purity nitrogen carrier gas at 1 Torr pressure for 30 min to outgas and achieved thermal equilibrium. The Pd ALD was performed using alternating exposures to palladium hexafluoroacetylacetonate (Pd(hfac)₂, Aldrich, 99.9%) and formalin (Sigma-Aldrich, HCHO 37 wt. % in H₂O) at 200 °C.¹ Timing sequence of a complete ALD cycle can be expressed as t₁-t₂-t₃-t₄, corresponding to the precursor exposure time, N₂ purge time, co-reactant exposure time and N₂ purge time, respectively. The timing sequence utilized for the Pd ALD was 100-300-100-300. Catalyst samples were prepared using 1, 3, and 10 Pd ALD cycles on the carbon black powder. The weight loading for each Pd ALD cycle is approximately 1 wt%.

Electrochemical characterization was carried out using a Swagelok-type cell^{4,5} composed of a lithium metal anode, electrolyte (1M LiCF₃SO₃ in tetraethylene glycol dimethyl ether

(TEGDME) impregnated into a glass fiber separator), and a porous cathode (13 mm diameter). The cathode was formed by casting a mixture of the as-prepared Pd/SPL carbon and binder in a molar ratio of 80:20 with the active material loading of about 1.0 mg/cm². The cells were sealed except for the Al grid window that exposed the porous cathode to 1 bar O₂ pressure. The electrochemical measurements were carried out using a MACCOR cycler. The discharge-charge performance was conducted in the voltage range of 2.0-4.5 V at a constant current of 100 mA/g, and the cell was maintained in 1 bar O₂ atmosphere to avoid any negative effects of humidity and CO₂. For comparison, a blank SPL carbon without any catalyst was also tested using the same cell configuration described above. We normalized the observed capacity by the weight of the carbon and catalyst for comparison in this study.

2 Characterization

The phase structures of the as-prepared Pd nanoparticles were identified using X-ray diffraction (XRD) with a wavelength of 0.774901 Å. These measurements were performed at beamline 11ID-D of Sector 11 at the Advanced Photon Source (APS) of Argonne National Laboratory. The X-ray specimens were prepared by tapping the powder into a Kapton capillary, which was then sealed at both ends. During the course of the measurements, a high-energy X-ray beam hit the sample horizontally, and a 2D detector (Pilatus 2M) was used to collect the X-ray diffraction profiles using transmission mode at a rate of one spectrum per minute. The 2D patterns were then integrated into conventional 1D patterns (intensity vs 2θ), and these data were analyzed using fit2D Software. Based on XRD peak broadening, the crystallite size of the sample was estimated using the Scherrer equation:

$$D_{hkl} = \frac{0.89\lambda}{\beta(2\theta) \cos(\theta)}$$

where $\beta(2\theta)$ is full width at half-maximum (FWHM) of the pure diffraction peak in radians, λ is the wavelength of the X-rays (0.774901 Å), θ is the diffraction angle, and D_{hkl} is the average diameter of the crystallite in Å. The cathode laminates after discharge were also characterized by HE-XRD to determine the formation of Li_2O_2 at beamline 11ID-C at the Advanced Photon Source (APS) of Argonne National Laboratory with X-ray wavelength of 0.774901 Å. The samples were completely covered with Kapton tape as a protective film in the glove box to avoid any side reactions from the air.

Pd K-edge (23.564 keV) X-ray absorption spectroscopy (XAS) was performed at the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The sample was loaded as a self-supporting wafer without binder in the channels (i.d. 4 mm) of a stainless steel multi-sample holder. The sample holder was then placed in the center of a quartz tube, which was equipped with gas and thermocouple ports and Kapton windows. The amount of sample used was optimized to achieve an XAS step height of about 0.5. The XAS spectra were recorded in transmission mode.

The Pd fraction was calculated by conducting Pd X-ray absorption near edge spectroscopy (XANES) linear combination fittings using Athena in the IFEFFIT (version 1.2.11) package. XANES reference spectra were collected using a metallic Pd foil and a Pd oxide sample. Standard procedures based on WINXAS 3.1 software were used to fit the data in the extended X-ray absorption fine structure (EXAFS) regime. The EXAFS coordination parameters were obtained by a least-square fit in q- and r-space of the isolated nearest neighbor, k^2 - weighted Fourier transform data.

Scanning transmission electron microscopy (TEM, JEOL JEM-2100F FEG FasTEM with an accelerating voltage of 200 KV) was employed to evaluate the morphology and particle size

of the ALD Pd catalysts. To prepare the TEM specimens, a dilute suspension was prepared by ultrasonically dispersing the Pd/C catalyst in ethanol for 5 min, and a drop of the suspension was placed onto a copper grid and dried. Particle size histograms were generated from the TEM images using software ImageJ.⁶

Samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos™ Axis Ultra DLD surface analysis instrument. The base pressure of the analysis chamber during these experiments was 3×10^{-10} Torr, with operating pressures around 1×10^{-9} Torr. Spectra were collected with a monochromatic Al K α source (1486.7 eV) and a 300 x 700 micron spot size. Prior to introduction into the load-lock vacuum chamber of the XPS instrument, all air-sensitive samples were loaded into an inert transfer module interfaced with the instrument. Samples were prepared in an Ar-filled glove box, with no more than 1 ppm O₂ and 1 ppm H₂O. Nonconductive samples showed evidence of differential charging, resulting in peak shifts and broadening. Photoelectron peak positions were shifted back toward their true values, and their peak widths were minimized by flooding the samples with low-energy electrons and ions from the charge neutralizer system on the instrument. Peak position correction was further corrected by referencing the C 1s peak position of adventitious carbon for a sample (284.8 eV, *PHI Handbook of Photoelectron Spectroscopy*), and shifting all other peaks in the spectrum accordingly.

Fitting was done by using the program CasaXPS. Peaks were fit as asymmetric Gaussian/Lorentzians, with 0-30 % Lorentzian character. The FWHM of all sub-peaks was constrained to 0.7-2.0 eV, as dictated by instrumental parameters, lifetime broadening factors, and broadening due to sample charging. With this native resolution set, peaks were added, and the best fit, using a least-squares fitting routine, was obtained while adhering to the constraints mentioned above.

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