**Porous and high conducting cathode material PrBaCo$_2$O$_{6-\delta}$: The bulk and surface studies for synthesis anomaly**


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**Figure S1** Variation of $\Delta Q/\Delta m$ with temperature (°C), the curves are showing a plateau around $T_{\text{decompose}}$ showing the thermal stability. This plateau is formed at higher temperature in ACR in comparison to SSR i.e. 232 °C – 372 °C in SSR and 247 °C – 385 °C in ACR.
In case of ACR, the calcined powder is sintered at 1050 °C, 1100 °C, 1150 °C and 1200 °C for 10 h. While in case of SSR, the calcined powder is sintered at 1050 °C, 1075 °C, 1100 °C for 10 h, 1150 °C. The samples synthesized through SSR have shown secondary phase of PrO$_{1.8}$ with the increase in sintering temperature and the sample melted at 1200 °C and 1300 °C (photographs of the samples shown in the manuscript Fig.2) whereas, in ACR, the secondary phase has diminished with the increase in sintering temperature and is minimum at 1150 °C and re-appears at 1200 °C.

**Figure S2** In case of ACR, the calcined powder is sintered at 1050 °C, 1100 °C, 1150 °C and 1200 °C for 10 h. While in case of SSR, the calcined powder is sintered at 1050 °C, 1075 °C, 1100 °C for 10 h, 1150 °C. The samples synthesized through SSR have shown secondary phase of PrO$_{1.8}$ with the increase in sintering temperature and the sample melted at 1200 °C and 1300 °C (photographs of the samples shown in the manuscript Fig.2) whereas, in ACR, the secondary phase has diminished with the increase in sintering temperature and is minimum at 1150 °C and re-appears at 1200 °C.
Figure S3 For the contribution of electronic states in the compounds, wide X-ray Photoelectron spectroscopy (XPS) spectrum for the optimized samples and indexing done using standard look up table. In the spectrum, it is very difficult to distinguish between Co and Ba peak, as they are highly overlapped ~ 800eV (inset (i)). Ba 3d peak is checked at 85 eV and is present in both the samples and near 800 eV peak belongs to Co. On reducing the data to 10 eV, it is showing the merging of peak at 0 eV for both the samples showing the samples should be highly conductive even than silver (inset (ii)).