Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.
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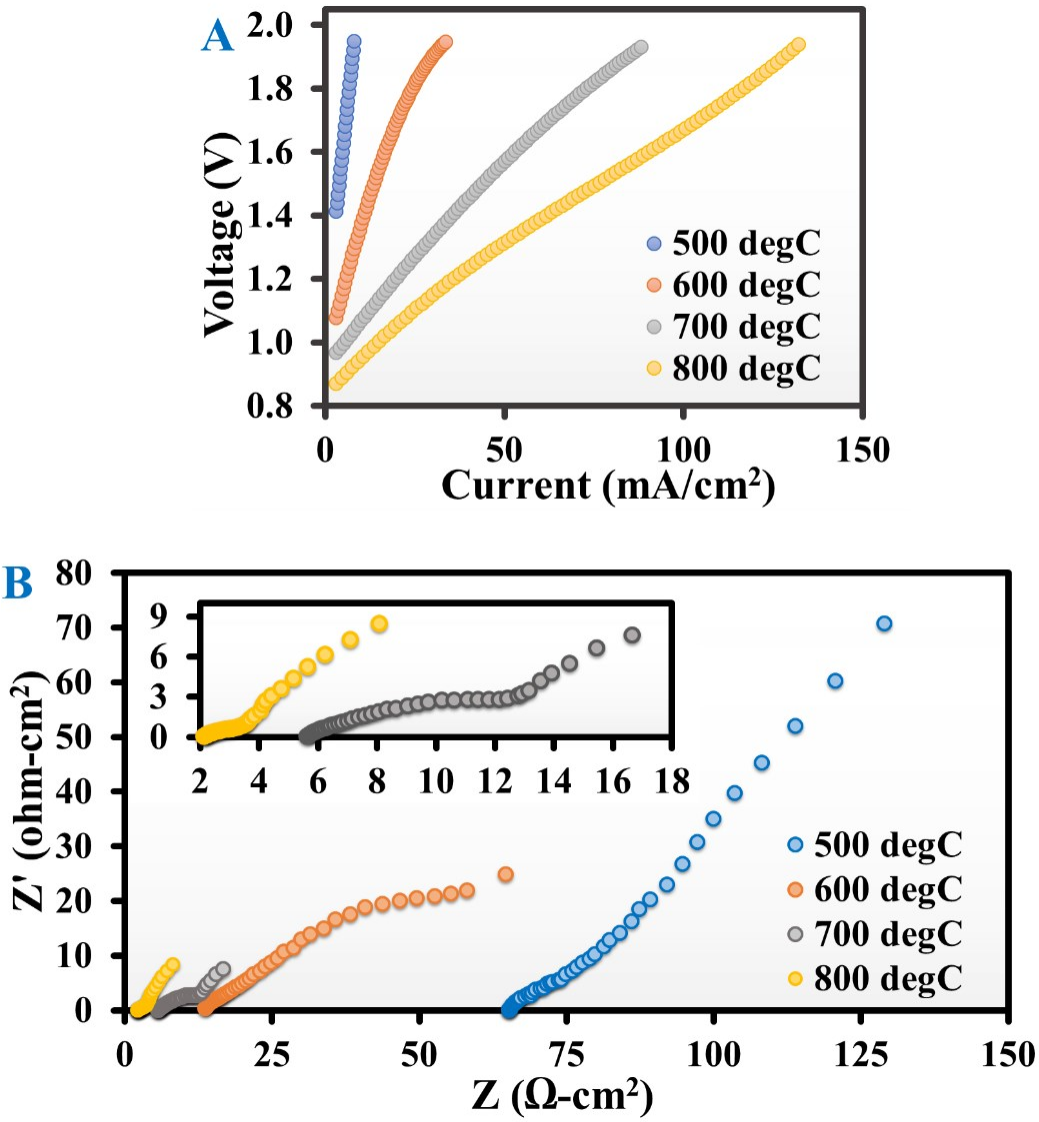

Figure S1. *(A) Current-voltage curves of a tubular solid oxide electrolysis cell with Ag-GDC composite electrode measured during electrochemical reduction of dry CO_2 at 500, 600, 700 and 800˚C and (B) corresponding electrochemical impedance spectra at open-circuit voltage*

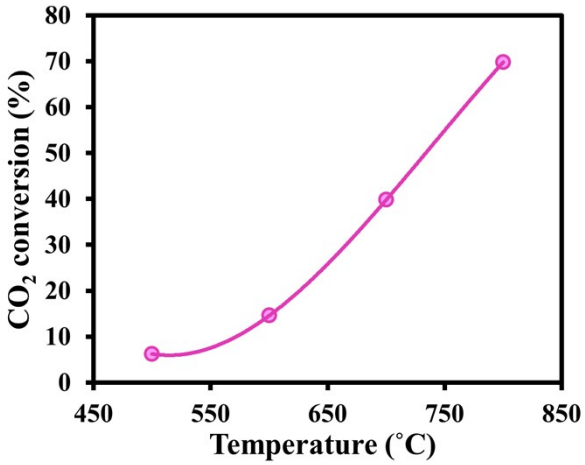

Figure S2. *CO_2 conversion at 500, 600, 700 and 800 ˚C at an applied potential of 1.5 V using Ag-GDC composite electrodes for dry CO_2 electrolysis*

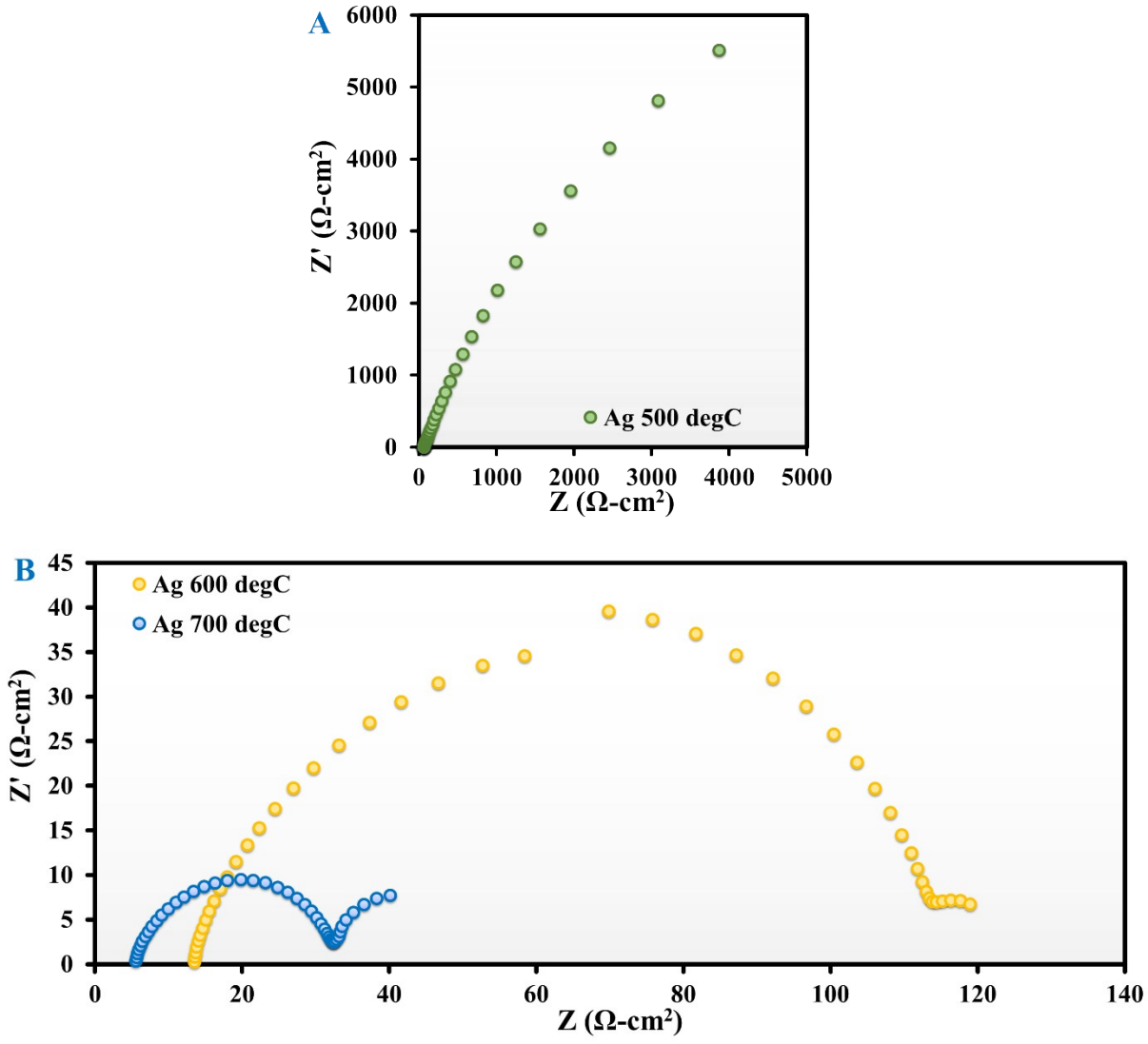

Figure S3. *Electrochemical impedance spectra measured at open-circuit voltage during electrochemical reduction of dry CO_2 at (A) 500 and (B) 600 and 700˚C*

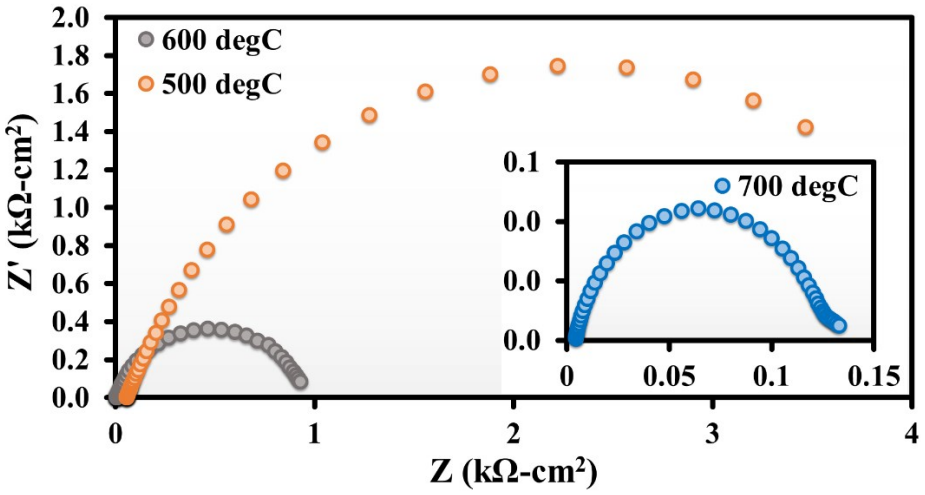

Figure S4. E*lectrochemical impedance spectra obtained at open-circuit voltage for a tubular solid oxide electrolysis cell with Ag electrode measured during electrochemical reduction of H_2/CO_2 mixture (4:1 v/v) at 500, 600, and (inset) 700˚C*

Physical characterisation of Ag-GDC composite electrode

Figure S5A shows the X-ray diffractogram of the Ag-GDC composite cathode before and after cell testing. Figure S5B shows the SEM images of as-prepared Ag-GDC electrode captured using a backscattered electron detector. As seen from the XRD reflections, the major phases present in both as-prepared and used electrodes were Gd-doped ceria (PDF 04-016-6174) and silver (PDF 00-004-0783). The XRD pattern of GDC exhibited typical diffraction peaks of fluorite-like structure. The lattice parameters of GDC and silver before and after in-situ methanation remained at 54.19 and 40.87 nm, respectively. This proves that the in-situ reduction of GDC during high-temperature electrolysis of either CO_2 or H_2/CO_2 mixture is a completely dynamic and reversible process that causes no deterioration or phase shift of the

GDC parent structure. No other minor phases were observed in the XRD patterns. The absence of any graphitic phase in the post-electrolysis sample proves that no coke deposition occurred.

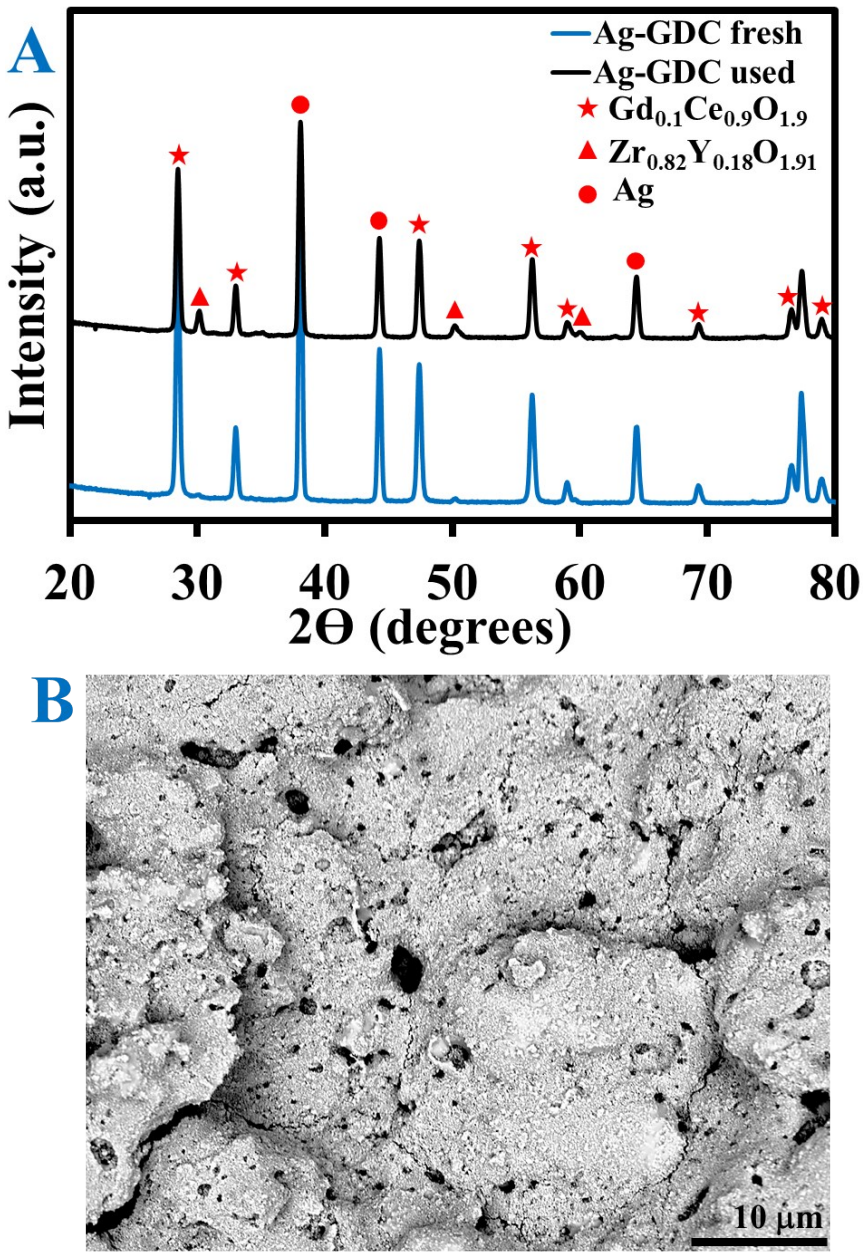

Figure S5. *(A) XRD patterns of Ag-GDC (blue solid line) as prepared and heat treated at 825 ˚C for 2 h, and after electrolysis (black solid line) of dry CO_2 (500-800˚C) and H_2/CO_2 mixture (4:1 v/v) (500-700˚C). Stars, triangles and circles indicate gadolinia doped ceria (PDF 04-016-6174), yttrium zirconium oxide (PDF 01-080-4012) and silver (PDF 00-004-0783)*

phases, respectively. (B) Scanning electron microscopy image of as-prepared Ag-GDC electrode