Oxygen Vacancy and Valence Engineering in CeO_2 through distinct sized ion doping and their impact on oxygen reduction reaction catalysis

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S1. Sample preparation

Undoped and the three different trivalent rare-earths (Y^{3+}, Eu^{3+} and La^{3+}) doped CeO_2 samples were synthesized via gel combustion method using cerium nitrate hexahydrate and urea as the oxidant and fuel, respectively. The fuel to oxidant ratio was kept at 2:1 for all the samples. The trivalent ion doping was carried out at two different molar concentrations of 2.5% and 5% w.r.t. the number of moles of ceria To prepare the Y^{3+} and La^{3+} doped ceria samples, stoichiometric amounts of lanthanum nitrate hexahydrate and yttrium nitrate were directly added to the precursor mixture, whereas to synthesize the Eu^{3+} doped samples initially a stock solution of Eu^{3+} was prepared by dissolving Eu_2O_3 in dil. HNO_3 and then requisite amount of that solution was added to the fuel-oxidant mixture. The sample solutions were heated under the IR lamp for approximately an hour to get converted into the gel form. The gel was then initially ignited for few minutes at 250 °C for the combustion of urea, followed by crushing, calcinations for three hours at 500 °C and then finally annealed at 800 °C for four hours.

S2. Electrochemical studies:

Table S1: The values of the different parameters obtained from fitting Nyquist impedance plots with equivalent circuit given in inset of figure 4(c)

Sample **Dopant in CeO_2**	**Resistance of the electrolyte** **(R_1 in ohm)**	**Resistance of catalyst** **(R_2 in ohm)**	**Constant phase element** **(Q_1 in F)**	**Electron transfer resistance** **(R_3 in ohm)**	**Double layer capacitance** **(C_3 in F)**
undoped	211	7153	9.4E-6	13000	3.21E-3
2.5% Y^{3+}	159	3589	5.59E-6	6591	7.5E-3
5% Y^{3+}	201	3166	5.21E-6	6193	7.62E-3
2.5% Eu^{3+}	166	5346	6.93E-6	10159	4.68E-3
5% Eu^{3+}	147	5591	7.58E-6	11201	4.91E-6
2.5% La^{3+}	212	3305	4.98E-6	6950	6.01E-3
5% La^{3+}	159	1725	4.03E-6	4131	5.49E-3