

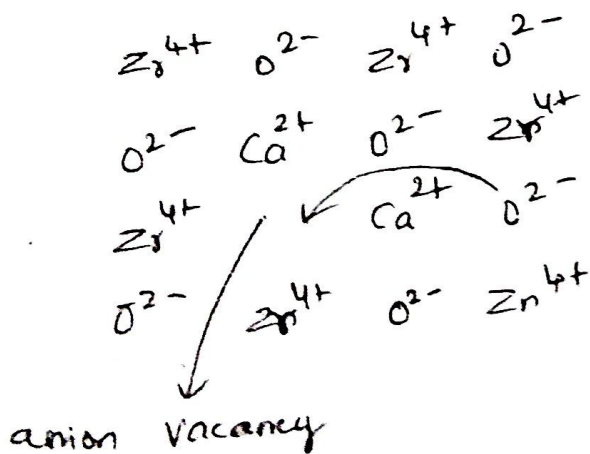
Extrinsic crystal defects:-

Vacancies can be introduced in a crystal by doping it with a selected impurity. Such created vacancies are known as extrinsic.

By introducing such defects, ionic conductivity can be induced in solids, such fast ion conductors have find applications as solid electrolytes in batteries, fuel cells & sensors.

For eg. let us consider oxide ion conductor:-

For eg. let us consider Zirconia, ZrO_2 . When it is doped with CaO (calcia), some of the Zr^{4+} ions in the crystal are replaced by Ca^{2+} ions. This leads to an increase in O^{2-} ions in the crystal. ~~For~~ To maintain electrical neutrality in the solid, equivalent number of O^{2-} ions leave their positions, introducing anion vacancies.



O^{2-} ion can ~~move~~ migrate from its lattice position to the vacant sites when electric field is applied.

Thus it behaves as an oxide ion conductor.

Similar effects are found when ZrO_2 is doped with Y_2O_3 (Yttria)

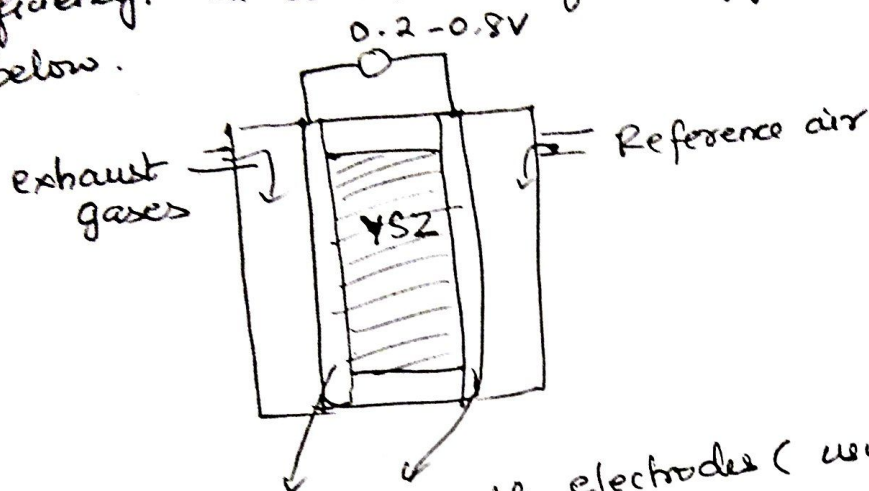
The solids are called as calcia stabilised zirconia or yttria stabilised zirconia (YSZ)

conductivity is maximum at low concentrations of dopants (15 to 25%)

Applications of oxide ion conductors —

① Oxygen sensor: —

The YSZ is used as solid electrolyte. The oxygen sensors are used in all automobiles to monitor the amount of oxygen in the exhaust gas. The amount of oxygen in the exhaust gas is a good indicator of engine combustion efficiency. The construction of an oxygen sensor is shown below.

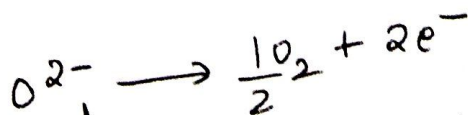


gas permeable electrodes (usually porous Pt electrodes)

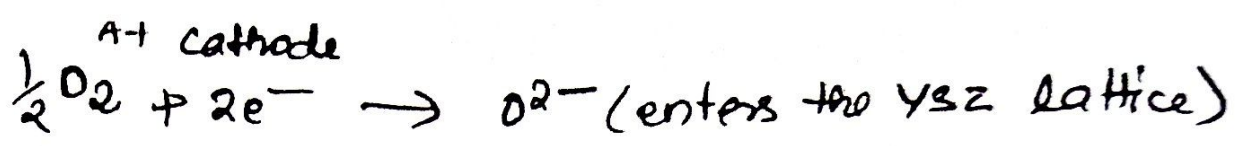
Due to the difference in oxygen concentration in the Reference air and in exhaust gases, a voltage will be generated. The voltage will be proportional to the concentration of oxygen in exhaust gas.

The role of YSZ is for oxide ion conduction from cathode to anode.

At anode (exhaust gas) where O_2 concentration is low, O^{2-} ions from the ~~electrode~~ solid electrolyte (YSZ) undergo oxidation to give O_2 gas at the Pt electrode

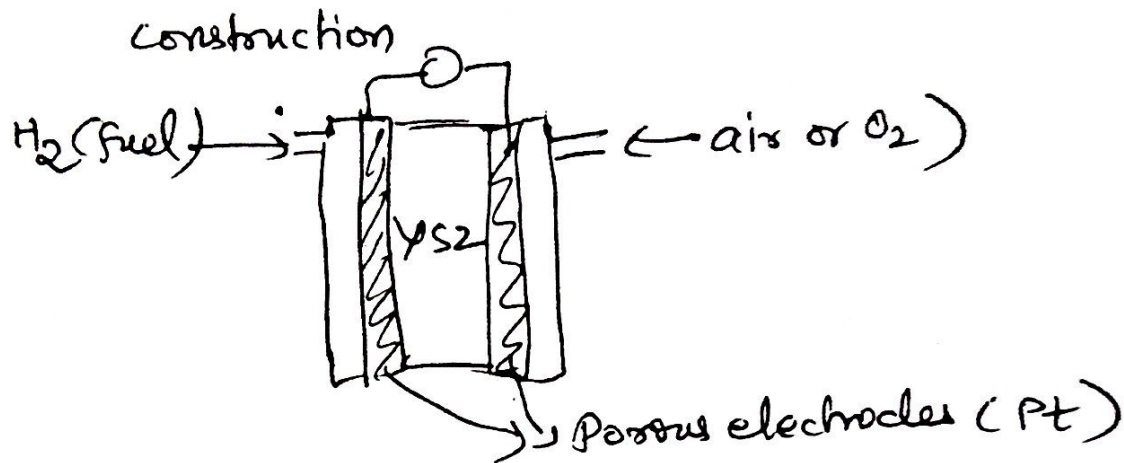


These ^{liberated} electrons migrate in the external circuit to the cathode (reference air) where concentration of O_2 gas is high. At the cathode $O_{2(g)}$ is reduced to O^{2-} ions which enter the crystal lattice of YSZ and these ions further migrate from cathode to anode

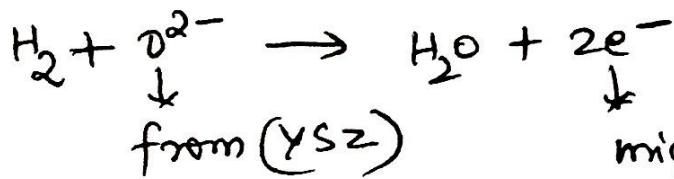


② Solid oxide fuel cell (SOFC)

In an SOFC a fuel is oxidised and the energy is converted into electrical energy. The YSZ is the solid electrolyte used for O^{2-} ion conduction.



At anode (fuel is oxidised)



migrate in the external circuit and reach the ~~anode~~ ^{cathode}

At ~~anode~~ cathode

