

Supplementary Information

Dysprosium based new Coordination Polymer and its Application towards Oxygen Reduction Reaction

Bandhana Devi^a, Rik Rani Koner^b and Aditi Halder^{a*}

^aSchool of Basic Sciences, Indian Institute of Technology, Mandi, Himachal Pradesh, India, ^bSchool of Engineering, Indian Institute of Technology, Mandi, Himachal Pradesh, India,

Crystal structure details-

Single crystals of Dy³⁺ suitable for X-ray diffraction were grown in DMF/H₂O via solvothermal method. Diffraction studies were performed on Agilent Technologies SUPERNOVA diffractometer with a CCD detector, using a Mo-K α radiation ($\lambda=0.71073\text{\AA}$). Crystal data was collected and reduced using the standard "CrysAlisPro" Software. The crystal structure was solved by direct method using SHELXS-97 and refining of structure was done by full matrix least squares using SHELXL-97. The positions of non-hydrogen atoms were located and refined anisotropically. After that hydrogen atoms were obtained from residual density map and refined with isotropic thermal parameters. The PLATON program was used to refine the disordered solvent molecules.

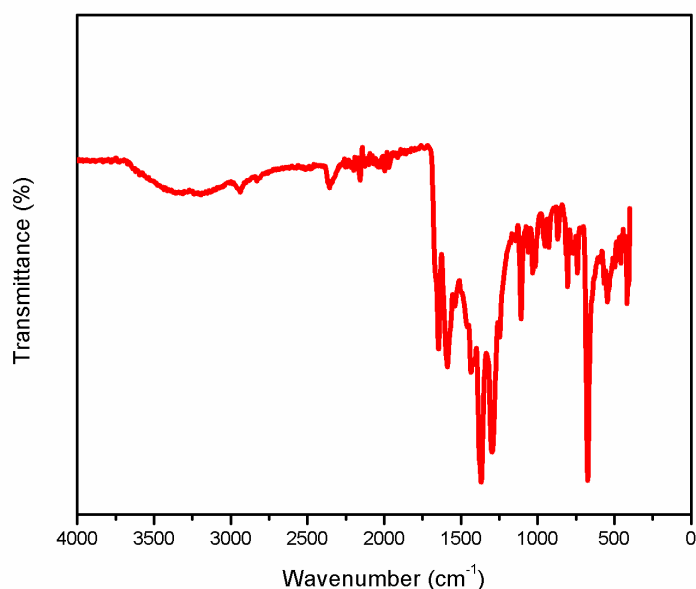
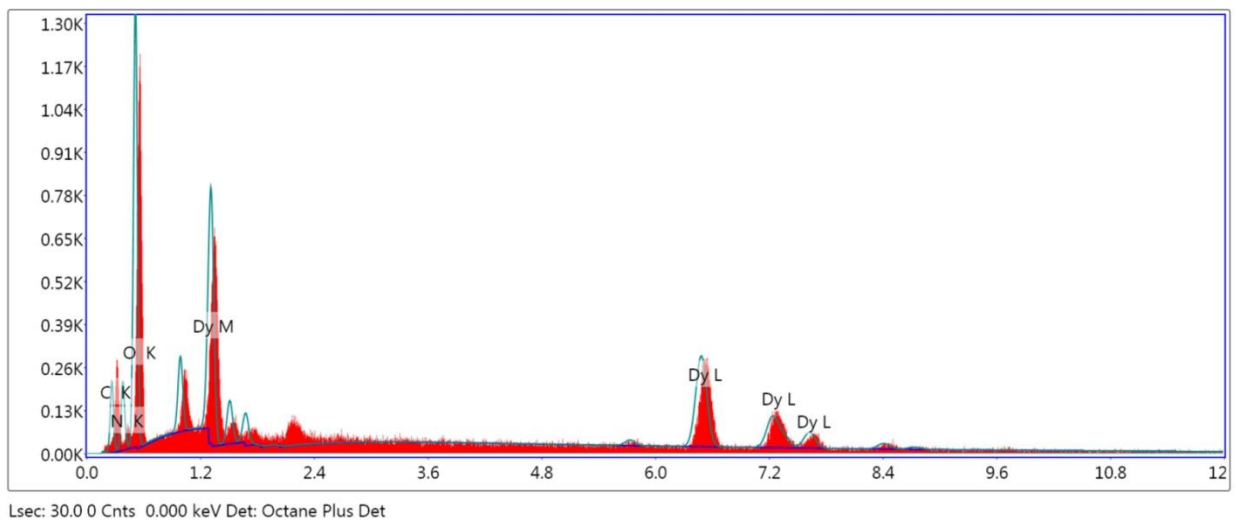
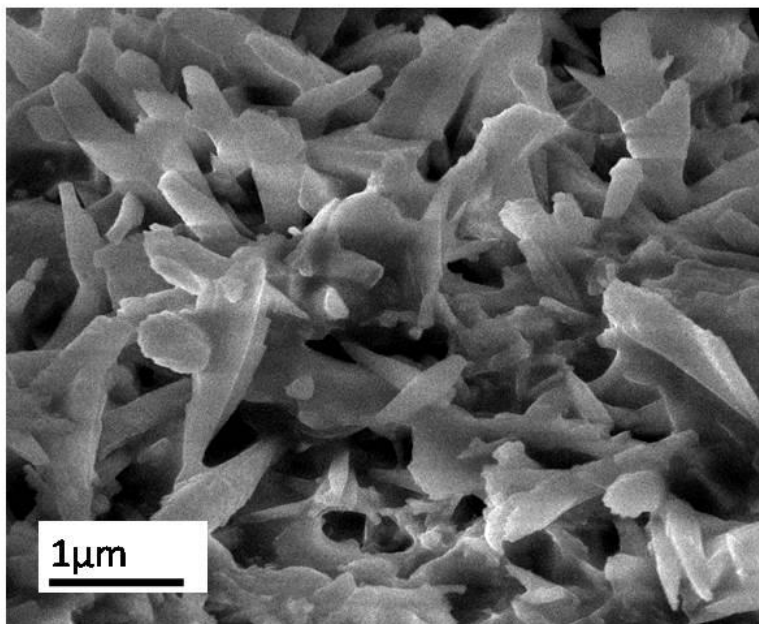


Fig. 1 FTIR Data of Dysprosium coordination polymer (Dy-CP)



Element	Weight %	Atomic %
C K	8.04	17.22
N K	9.62	17.66
O K	35.95	57.78
DyL	46.40	7.34

Fig. 2 (a) shows SEM image of Dysprosium coordination polymer (Dy-CP) 2 (b) shows EDS data of Dy-CP.

SEM image shows that particles are elongated, plate like in structure.

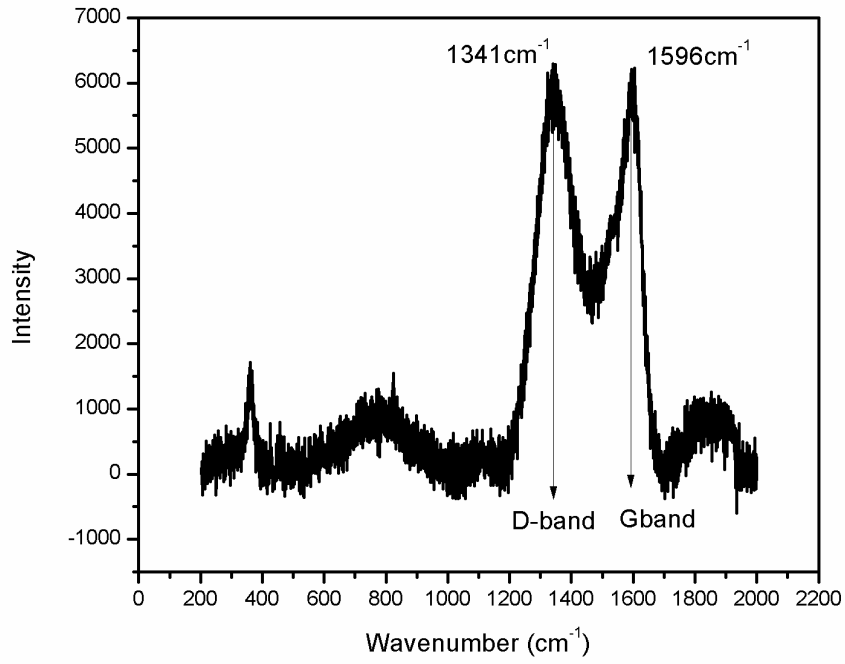


Fig. 3 Raman data of Dy-CP annealed at 800°C.

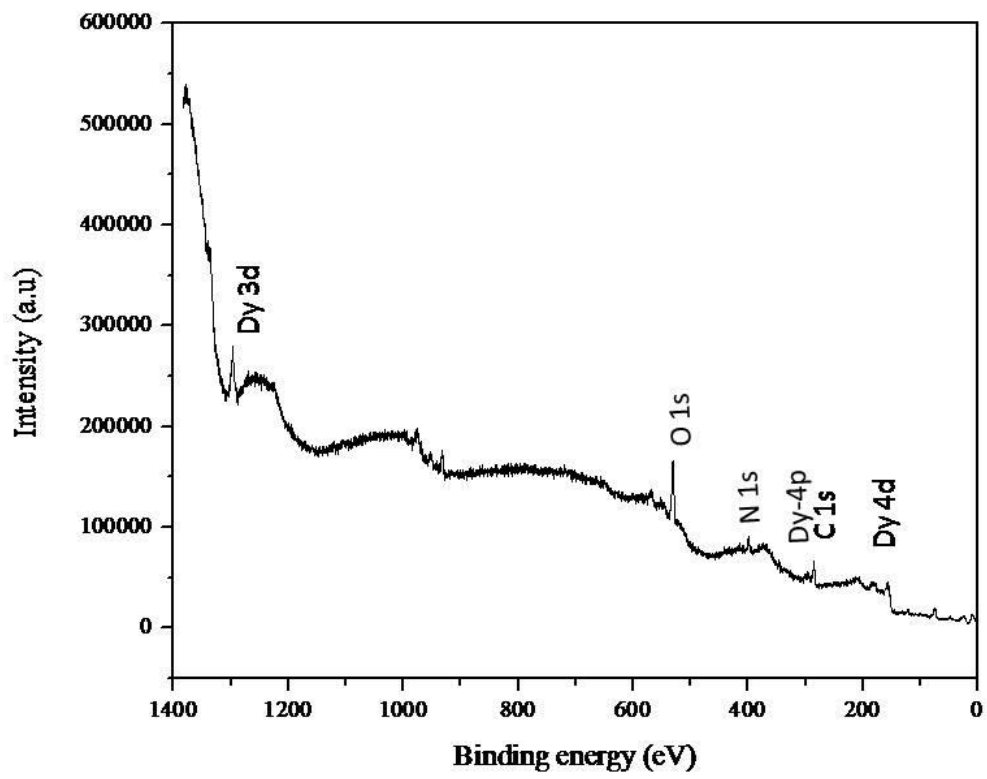


Fig. 4 XPS spectrum (Wider scan of Dy-CP annealed at 800°C.

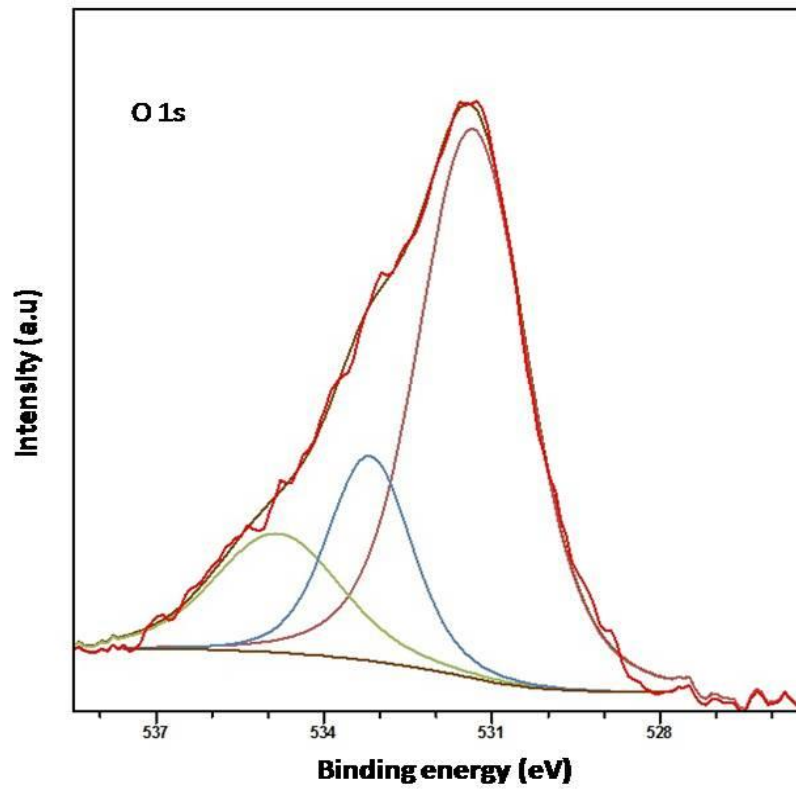
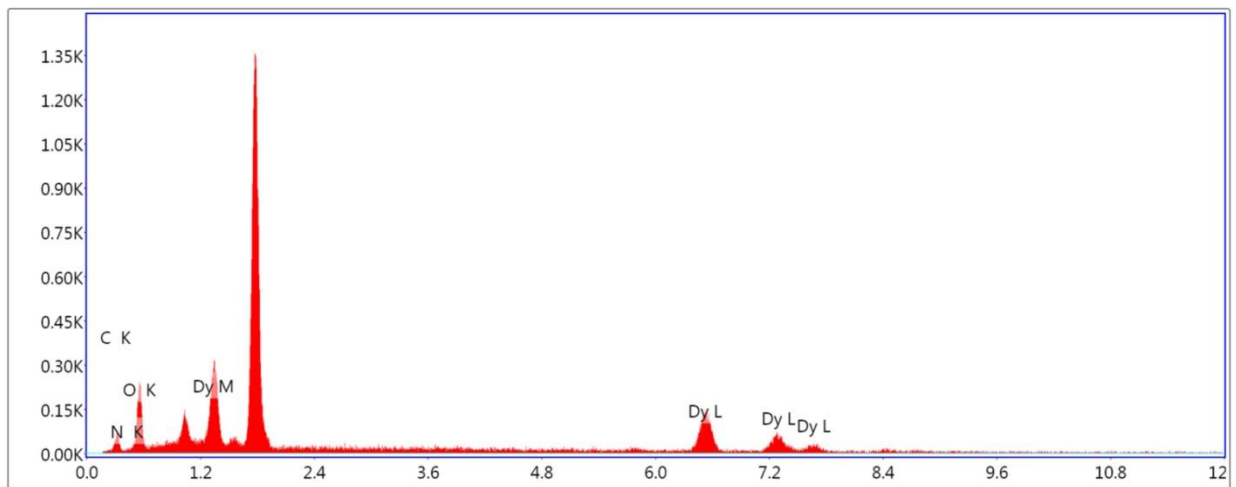


Fig. 5 XPS spectrum of O1s

The O1s spectrum is deconvoluted into three peaks at 531.3, 533.2 and 534.7 eV which correspond to Oxygen bonded to Dysprosium, oxygen bonded to carbon and adsorbed hydroxides or carbonates.



Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Plus Det

Element	Weight %	Atomic %
C K	7.66	22.43
N K	6.46	16.23
O K	21.57	47.42
DyL	64.31	13.92

Fig. 6 EDAX spectrum of Dy-CP annealed at 800°C.

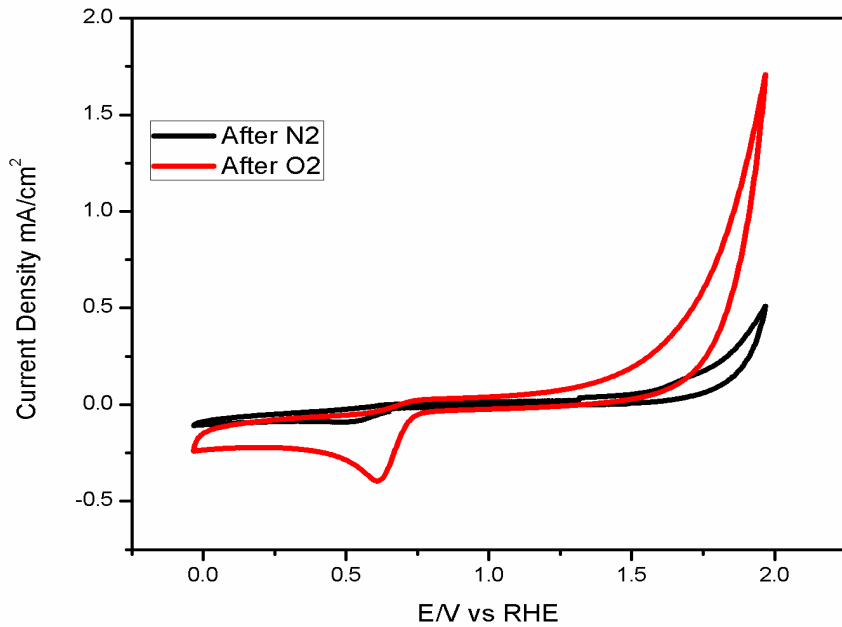


Fig. 7 Shows the CV data of Dy-CP

CV data shows that Dy-CP is ORR active material. There is a small reduction peak of material in N_2 saturated solution and there is a well defined reduction peak in O_2 saturated solution (0.1M KOH) at 0.73V

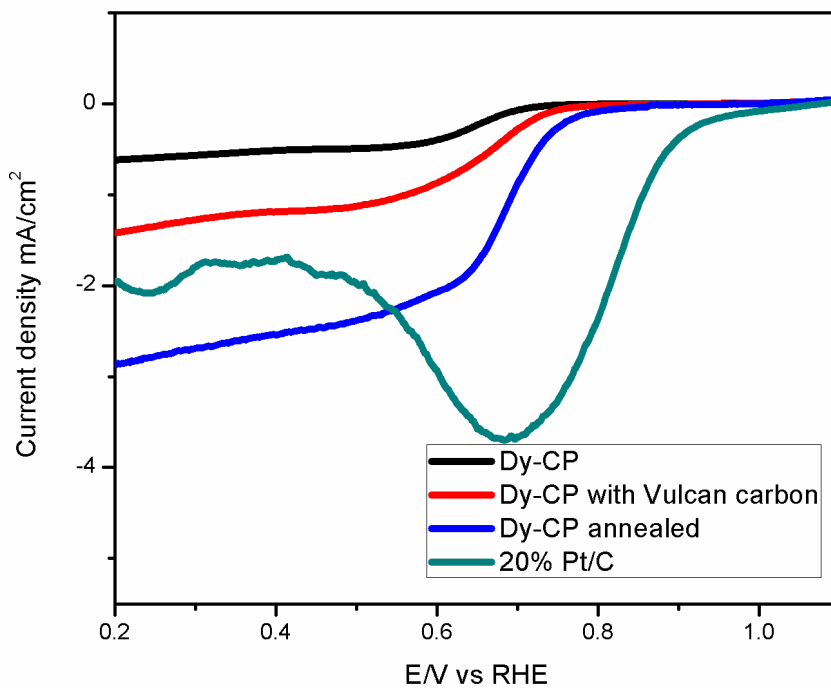


Fig. 8 Shows overall comparison of ORR activity of Dy-CP at 1600rpm.

The comparison of ORR activity at 1600rpm indicates that ORR activity increases after adding Vulcan carbon to Dy-CP as a support material, but on annealing Dy-CP at $800^{\circ}C$, ORR activity further increases without Vulcan carbon. So, the increasing order of ORR activity is-Dy-CP< Dy-CP with Vulcan carbon< annealed Dy-CP.

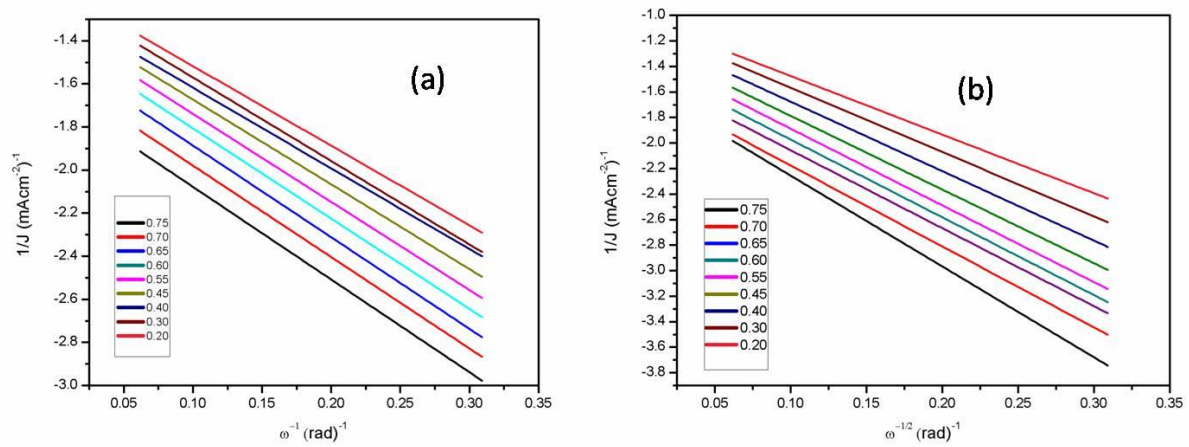


Fig. 9 Shows K-L plot for (a) Dy-CP (b) Dy-CP with Vulcan carbon.

The linearity of K-L plots indicates the first order kinetics.

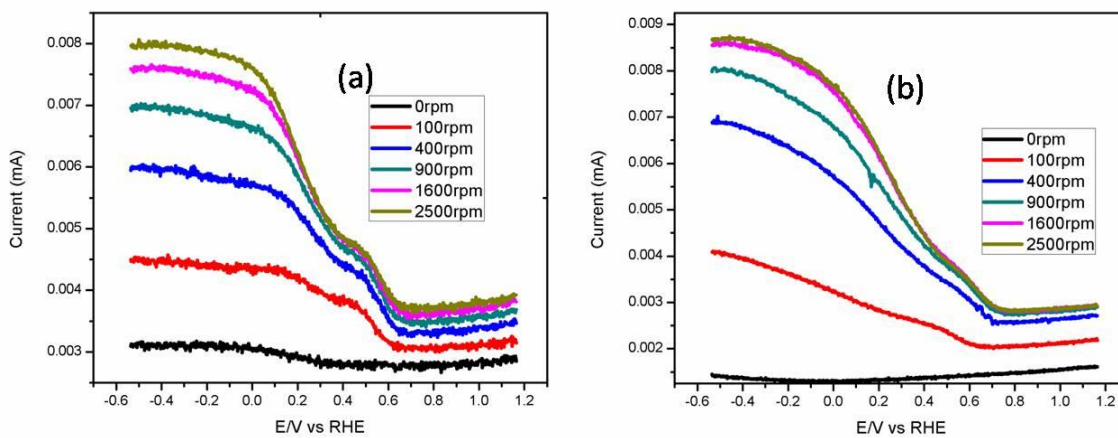


Fig. 10 Shows Ring current for (a) Dy-CP (b) Dy-CP with Vulcan carbon as a support.

For non- annealed Dy-CP, we got a 4e⁻ mechanism-

Dy- CP	Potential	n=No. of electrons involved
Dy- CP	0.78	3.2
Dy -CP	0.76	3.6
Dy -CP	0.72	3.7
Dy -CP	0.70	3.7
Dy -CP	0.66	3.9

For annealed Dy-CP, we got a mixed mechanism (2e⁻ and 4e⁻)

Sample	Potential	n=No. of electrons involved
Dy -800	0.78	2.8
Dy- 800	0.76	2.9
Dy- 800	0.72	3.3
Dy -800	0.70	3.2
Dy 800	0.66	3.4
Dy 800	0.64	3.6
Dy 800	0.62	3.8
Dy 800	0.60	3.9

For non annealed sample with Vulcan carbon as a support, (n) electron transfer no. came out to be four. So, it follows four electron mechanism -

Sample	Potential	n=No. of electrons involved
Dy-CP with vulcan carbon	0.78	3.98
Dy-CP with vulcan carbon	0.76	3.99
Dy- CP with vulcan carbon	0.72	3.99
Dy -CP with vulcan carbon	0.70	3.98
Dy- CP with vulcan carbon	0.66	3.99
Dy -CP with vulcan carbon	0.64	4
Dy- CP with vulcan carbon	0.62	3.99

Fig. 11 shows the detailed mechanism of Dy-CP,Dy annealed at 800°C and Dy-CP with Vulcan carbon.

The detailed mechanism shows that in Dy-CP annealed at 800 °C , n value changes from 2.8 to 3.9 and the overall value is about 3.6 which is close to 4. It means that here some amount of HO_2^- is generated as an intermediate which is then further reduced to OH^- .