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Electrochemistry of Two Hexa-iron-sulfur Carbonyl Clusters

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The electrochemical behaviours of two hexa-iron clusters **1** and **2** are investigated by using cyclic voltammetry. The results show that cluster **1** capture one electron more readily than cluster **2** and the central 6CO can be reduced easier than sub-site 6CO and 5CO in the cluster **1**, which are associated with that the electron withdrawing effect of 5CO sub-unit by Fe-S bond is more significant than 6CO bond linkage by S. This conversion can be reversed by continuously purging CO through the solution of the cluster **1**.

Key Words: Hexa-iron-sulfur carbonyl clusters, Electrochemistry, Electron withdrawing effect.

INTRODUCTION

Fe-S clusters are found in ferredoxins and other electron transfer proteins, hydrogenases, nitrogenase and in many more proteins and play important role in electron-transfer, catalysis, gene-regulation and the sensing of iron and oxygen[1]. It is known that active centre, also called the H-cluster of [FeFe]-hydrogenase consists of an $\{Fe_2S_2\}$ unit and an $\{Fe_4S_4\}$ cubane, they are jointed together through a bridging cysteinate[2-4] (Fig. 1).

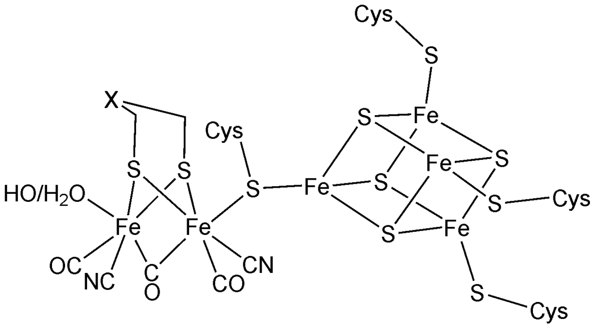
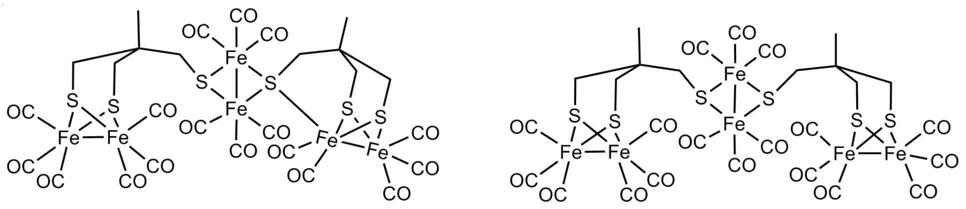


Fig. 1. Schematic view of the H-cluster of the [FeFe]-hydrogenase (X = CH_2, NH or O)

Earlier, we reported[5] synthesis, characterization of two hexa-iron clusters **1**, **2** with $\{Fe_2S_2(CO)_x\}$ (x = 5 or 6) fragments and investigation into their inter-conversion and their structure are shown in Fig. 2. Here we continue to investigate their electrochemistry behaviours.



1 **2**

Fig. 2. Structure of the clusters **1** and **2**

EXPERIMENTAL

The methods of preparation and determination of the clusters **1** and **2** were followed as reported[5].

Electrochemistry was carried out under argon atmosphere or CO atmosphere in freshly dried dichloromethane at a scanning rate of 100 mVs^{-1} on Autolab Potentiostat 30. Conventional three-electrode system was employed in which vitreous carbon disk (ϕ = 1 mm) was used as working electrode, vitreous carbon strip as counter electrode and Ag/AgCl (Metrom) as reference electrode whose inner reference solution is composed of 0.05 M [NBu_4]Cl and 0.45 M [NBu_4]BF_4. In dichloromethane, the electrolyte concentration is 0.5 M [NBu_4]BF_4. All potentials were quoted against ferrocenium/ferrocene couple, whose half-wave potential is 0.55 ± 0.01 V against the above Ag/AgCl reference electrode in dichloromethane. The solvent was purchased from Alfa Asear and freshly distilled over P_2O_5 before use.

RESULTS AND DISCUSSION

Cyclic voltammograms of the clusters **1** under Ar and **2** under CO atmospheres are presented in Fig. 3. The cluster **1** exhibits three irreversible reduction processes at -1.39, -1.81 and -1.96 V, respectively with the first one well away from the other two processes (Fig. 3 dash line). As revealed by its structure (Fig. 2, left), the central 6CO sub-unit is flanked by both one 6CO and one 5CO sub-units. It is known that the di-iron sulphur carbonyl motifs show electron withdrawing nature[6]. Thus the metal-metal bond of the central sub-unit will have the lowest electron density compared to the other two metal-metal centres and thus the reduction at -1.39 V is assigned to one electron reduction of the central di-iron core. Due to the electron-withdrawing effects from its two satellite di-iron sub-units, this reduction potential shifts positively by *ca.* 250 mV compared to that of simple complex, for instance, [Fe_2(pdt)$(CO)_6$][7,8]. The remaining two reductions at -1.81 and -1.96 V, are assigned to the 6CO and 5CO sub-units, respectively. Accumulation of electronic effects from successive reductions lowers the potentials for the two di-iron centres by over 100 mV compared to those of the complexes of {$Fe_2S_2(CO)_6$} and {$Fe_2S_2(CO)_5$} moities[6,7,9] **Scheme-I** (left panel).

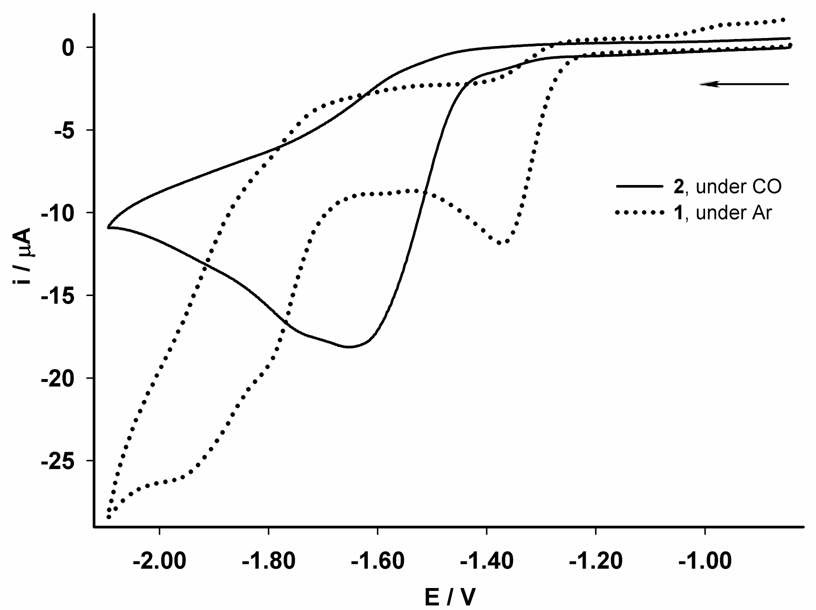
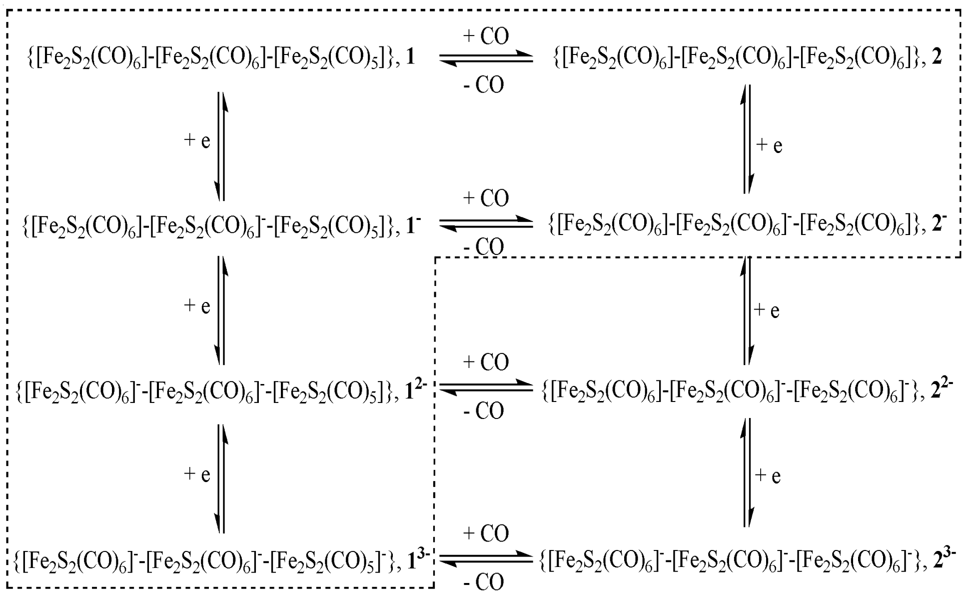


Fig. 3. Reduction part of cyclic voltammograms of the clusters **1** (C = 3.8 mM) in argon atmosphere and **2** (C = 2.7 mM) under CO atmosphere in dichloromethane at 298 K



Scheme-I: An overall electrochemical pathways for **1** and **2**, for clarity reason, no chemical processes are presented except for the processes involving CO binding/cleaving

As shown in Fig. 3 (solid line), the cluster **2** in dichloromethane exhibits a broad irreversible reduction peak centred at *ca.* -1.70 V under CO atmosphere. Close examination can reveal that it is multiple processes. As shown in its structure, Fig. 2 (right), there are three sub-units of 6CO sub-unit and the central one is surrounded by another two 6CO sub-units through two bridging S atoms. Based on the same argument as described above for the electrochemistry of **1**, it is suggested that the central sub-unit is first reduced at a potential more negative than that for the cluster **1** and close to the reduction potentials for other simple complexes with $\{Fe_2S_2(CO)_6\}$-core[7, 9]. The closely followed processes are attributed to the successive reductions of the two satellite 6CO sub-units, **Scheme-I** (right panel).

Cyclic voltammograms of the cluster **1** under CO atmosphere and the cluster **2** under Ar atmosphere are shown in Figs. 4 and 5 (dotted line), respectively. From Fig. 4 can be seen, the peak current of -1.39 V decreases gradually with the time extending under CO atmosphere, whereas the peak current of -1.60 V grows up. However, from Fig. 5 (dotted line) can be seen that the electrochemistry of the cluster **2** under argon atmosphere has the features of the cluster **1** and the change is not significant even with longer time. All above these indicates the conversion from **1** to **2** involving one CO uptake is much faster than its reverse process.

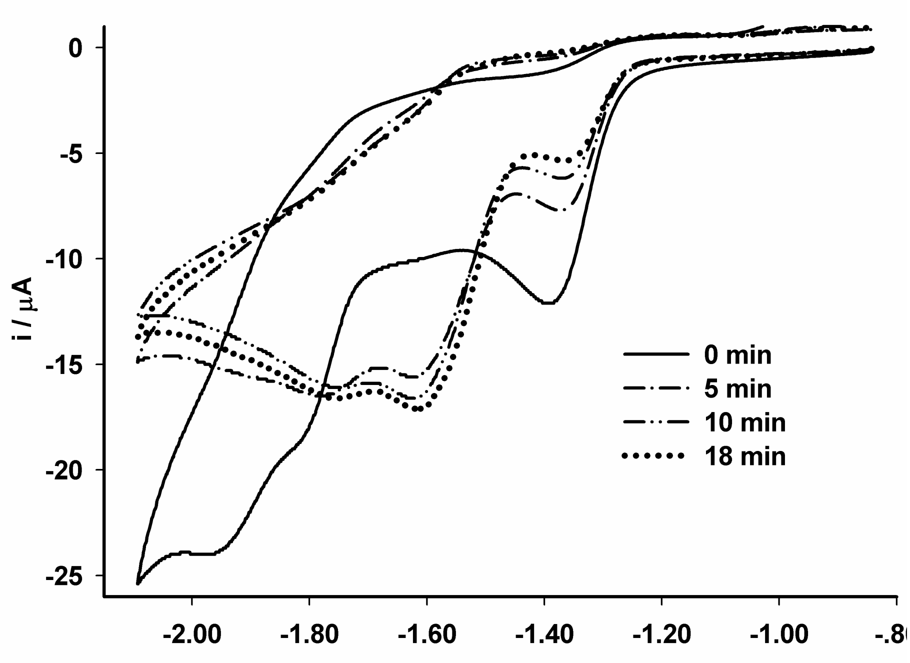


Fig. 4. Changes in cyclic voltammograms when the solution of **1** is purged with CO in dichloromethane at room temperature

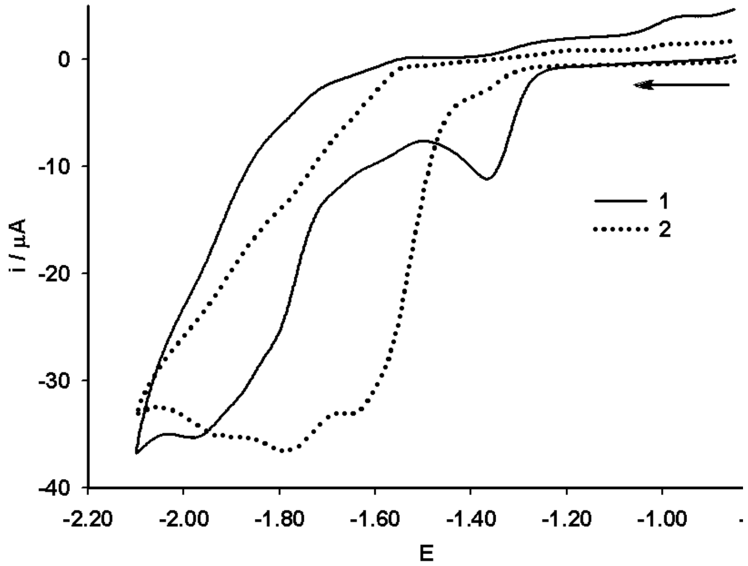


Fig. 5. Cyclic voltammograms of the clusters **1** and **2** under argon atmosphere in dichloromethane at room temperature

It is already reported[5] that the neutral cluster **2** undergoes conversion to the cluster **1** *via* the nucleophilic attack of one of the bridging S atom on the proximal Fe(I) of its neighbouring 6CO sub-unit and upon the reduction of the central sub-unit, the conversion between **2**$^{-}$ and **1**$^{-}$ is more feasible as the S atom is more nucleophilic, which is supported by DFT calculations. But the presence of CO, the conversion from **2** to **1** is essentially suppressed and so is the conversion from **2**$^{-}$ to **1**$^{-}$. The overall electrochemistry for both clusters is outlined in **Scheme-I**. For simplicity, chemical processes following those reductions are not presented.

Further scanning to cluster **1** at positive scope reveales that there are two irreversible oxidation waves at *ca.* + 0.45 V and + 0.78 V (Fig. 6, solid line), whereas there is a significant irreversible oxidation peak at + 0.85 V in the cluster **2**. In cluster **1**, the first oxidation wave is assigned to sub-site 5CO. In cluster **2**, the strong peak is associated with the three 6CO units accepting electrons. These are also associated with their electron-withdrawing effect to each other.

Conclusion

The electrochemistry of two hexa-iron clusters **1** and **2** were investigated. Due to the metal-metal bond of the central sub-unit has the lowest electron density compared to the other two metal-metal centres, the first reduction wave of the cluster **1** is assigned to one electron reduction of the central di-iron core. The two clusters undergo interconversion through concomitant Fe-S formation and CO cleavage or *vice versa* and the conversion from **1** to **2** involving one CO uptake is much faster than its reverse process.

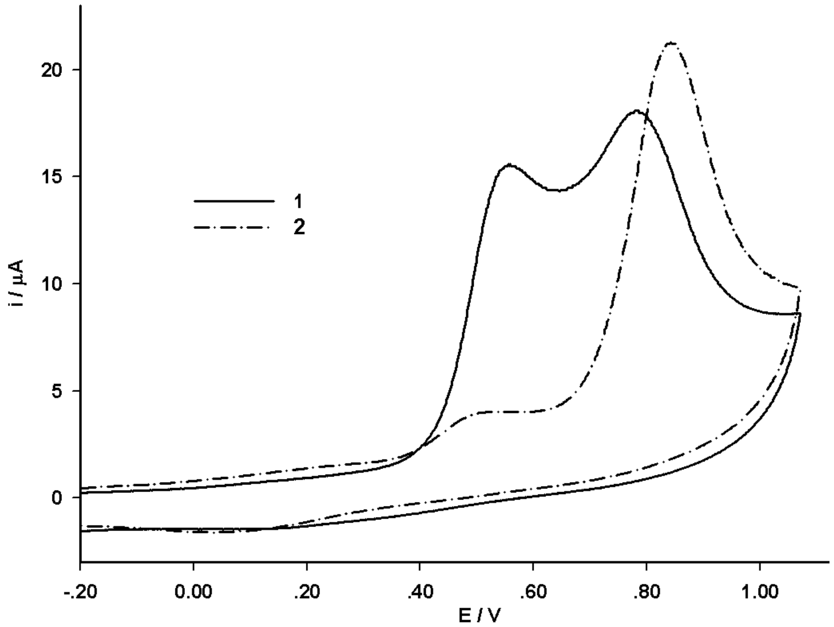


Fig. 6. Oxidation peaks of the clusters **1** (C = 2.3 mM) and **2** (C = 2.7 mM) under argon atmosphere in dichloromethane at room temperature

REFERENCES

1. R.H. Holm, P. Kennepohl and E.I. Solomon, *Chem. Rev.*, **96**, 2239 (1996).
2. J.W. Peters, W.N. Lanzilotta, B.J. Lemon and L.C. Seefeldt, *Science*, **282**, 1853 (1998).
3. Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian and J.C. Fontecilla-Camps, *Struct. Folding Design*, **7**, 13 (1999).
4. A.S. Pandey, T.V. Harris, L.J. Giles, J.W. Peters and R.K. Szilagyi, *J. Am. Chem. Soc.*, **130**, 4533 (2008).
5. W. Zhong, G. Zampella, Z. Li, L. De Gioia, Y. Liu, X. Zeng, Q. Luo and X. Liu, *J. Organomet. Chem.*, **693**, 3751 (2008).
6. C. Tard, X.M. Liu, S.K. Ibrahim, M. Bruschi, L. De Gioia, S.C. Davies, X. Yang, L.S. Wang, G. Sawers and C.J. Pickett, *Nature*, **433**, 610 (2005).
7. A. Winter, L. Zsolnai and G. Huttner, *Z. Naturforsch.*, **37B**, 1430 (1982).
8. S.J. Borg, T. Behrsing, S.P. Best, M. Razavet, X.M. Liu and C.J. Pickett, *J. Am. Chem. Soc.*, **126**, 16988 (2004).
9. M. Razavet, S.C. Davies, D.L. Hughes, J.E. Barclay, D.J. Evans, S.A. Fairhurst, X.M. Liu and C.J. Pickett, *Dalton Trans.*, 586 (2003).

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