Beneficiation opportunities for osmium: A review

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Abstract. This review summarises the safe production of osmium and its compounds and its functionality from both the chemistry and materials perspectives. A review of the available data shows that there is a lot of potential for osmium (II) compounds to be used for traffic signalling as molecular signal gates using electrochemical generated power. Osmium (II) compounds can also be used for biomedical applications such as the development of anticancer drugs. Organic compounds of osmium have also been found to possess excellent electrochemical properties which are useful for redox flow battery. Different synthesis routes to produce these compounds and implementation thereof into the redox flow battery systems are described in details. This review of osmium and its compounds possess a variety of correlated properties with a potential to put an emergent demand on osmium for various applications.

1. Introduction

Osmium (Os) is one of the platinum group metals. Its reserves are mostly found in South Africa, Russia and North America. It has not been used in most applications because of its tendency to produce a dangerous compound called osmium tetroxide (OsO₄), which when inhaled it causes harm. The slow reaction of Os powder with oxygen gives off detectable amounts of OsO₄ vapour [1,2].

The OsO₄ is highly toxic with low contents of about 10⁻⁷ g.m⁻³ causing lung congestion, skin damage and severe eye damage. A harmful contamination of the air can be reached very quickly on evaporation of this substance at 20°C. It is a strong oxidant and it reacts with combustible and reducing materials. It is therefore necessary to come up with safe synthesis route of osmium-based compounds in order for osmium to be useful [1,2].

Osmium is commercially recovered from the platinum group metal (PGM) ores. Platinum and palladium are the most commercially used and osmium is the least used of the PGMs. South Africa, Russia and Canada have approximately 98% of known global PGM reserves. In South Africa the approximate distribution of operating costs during PGMs recovery for each stage are as follows: 72% mining, 9% smelting and 9% refining. It has been reported that osmium has been left piling in the tailing dams and waste streams. This project will focus on evaluating how much of osmium is mined as part of total PGMs and whether or not that amount can be of any use, starting with this review [3,4].

Osmium has a very high bulk modulus of 383-462 GPa, which is very close to that of diamond which is 446 GPa. Compressibility of osmium is generally low and is dependent on its pressure volume-temperature behaviour. It has a hexagonal-close packed structure. However, its mechanical and physical properties are unique. It is very hard, extremely dense and brittle which makes it difficult to process for metallurgical purposes [5–12]. Several properties of osmium and its compounds from
both chemistry and materials perspectives have been reviewed in the current paper and the possible applications are discussed.

2. Safe synthesis of osmium-oxide compounds

Osmium tetroxide is the most useful compound of osmium. This compound is in demand for use as a catalyst for research purposes, although it is highly reactive in air and therefore dangerous. It has therefore been a difficult process to synthesize this compound and to find more suitable applications [13]. There are other osmium oxide compounds which have been explored fully by the researchers. Yamaura et al. [14] studied the high pressure and temperature synthesis of osmium oxides using belt-type high-pressure apparatus. The synthesised solid-state compounds were then characterised for consideration for possible applications.

The use of this method avoided possible man exposure to highly toxic OsO₄. Figure 1 shows the apparatus of belt-type high-pressure apparatus that were used at NIMS, Hokkaido University-Japan. The synthesis was performed by first sealing a mixture of high-purity starting material in Pt capsule in an argon filled glove box. The capsule was then statically and isotropically compressed to a pressure of 6 GPa in the belt-type high-pressure apparatus. This was followed by heating at temperature 2000℃ for 1 hour [9,14].

![Figure 1. Assembled views of a belt-type high-pressure apparatus and sample cell [14]](image)

The pellets obtained were then characterised using X-Ray Diffraction. His [14] results showed that there is a vast opportunity for synthesis of osmium oxides safely. Successional synthesis of Os oxides was performed, for example, LiOsO₃ using similar method of belt-type high pressure. However there was no success regarding the target applications which were magnetism and conductivity. These studies showed that there is a promising future for further research for Os oxide compounds and their applications [9]–[12].

3. Traffic signals

Traffic signals are developed by information programming. The chemically encoded information leads to the generation of optical output signal which in turn give rise to the development of molecular level logic gates such as AND, OR, NOR, INHIBIT, XOR, YES, NOT and XNOR. The physical integration of these molecular logic gates are related to functional integration and processing of binary data in conventional microprocessor based systems. The conventional system uses mostly silicon based technology, but miniaturisation is limited up to nanometer scale. Thus, construction of new materials that are suitable for information storage and retrieval at the molecular level have been developed to overcome the limit [15,16].
Mardanya et al. [15] utilised osmium (II) complexes based on pyrene-biimidazole ligand. This complex had remarkable photophysical properties which arise due to metal-to-ligand charge transfer transition. In order to mimic the molecular trafficking mechanism, three chemical inputs were chosen: CN⁻ (Input 1), H₂PO₄⁻ (Input 2) and H⁺ (Input 3). It was observed that the extent of absorption spectral changed substantially with variation of inputs. A designation was given for each output absorption signal generated at different inputs, that is, CN⁻ has the green signal, H₂PO₄⁻ has the yellow signal and H⁺ has the red signal [15]. This provides osmium with a promising future for the actuator applications.

4. Anti-cancer drugs discovery

Due to the chemical properties of osmium, it has been a metal of interest when it comes to research for anti-cancer compounds. Its complexes have become increasingly important in the field of tumor-inhibiting metal species in the past years. It was established that the synthesis of Os (II) complexes demonstrated that they have a comparable cancer cell cytotoxicity to cisplatin [17].

The focus in recent years has been on the development of chemotherapeutic osmium compounds, which are organometallics with arene or cyclometallated ligands. The studies showed that the arene complexes have a limitation because they are not stable in water or air. However, the problem was resolved by modulating the steric and electronic properties of the substituents on chelating ligands to control the kinetics and thermodynamics of osmium drugs in aqueous media. In addition, metal complexes of osmium in low oxidation state (+2, +3 and +4) have anti-cancer properties by inducing cell death via DNA targeting [17,18].

Recently, the first osmium complexes to induce cell death via endoplasmic reticulum stress were synthesised. Os (VI) nitride compounds bearing bidentate ligands showed that small modifications to ligands periphery induced completely different cellular responses, which lead to genomic arrests that could be chemotherapeutic [18,19].

5. Biosensors

Lithium and alkaline electrolytes batteries have long been accepted and used to power implantable and semi-implantable devices, such as insulin pumps, neurostimulators and pace makers. These batteries provide power through an internal chemical reaction. The modern technology seeks to improve these batteries by shrinking battery size and enhancing lifetime [20].

This could be achieved by developing medical device that takes advantage of fuel cells that derive their fuel and oxidant from the in-vivo environment. With such development, there will be no requirements to provide anode and cathode power generating capacity within the device, allowing miniaturisation. This therefore presents a new innovative direction in the medical device technology [20].

Osmium-based redox complexes have been found to be excellent electron transfer mediators due to their relative stability in both oxidised and reduced states and their fast electron exchange rate compared to other metal based mediators. Osmium based complexes can be widely explored for a range of applications such as redox catalysts and mediators due to ease of synthetic variation of structure. Polyvinyl imidazole (PVI) bound osmium polypyridyl series of redox polymers have been widely used in mediated enzyme electrodes for application such as biosensor and enzymatic fuel cell electrodes for power generation [20]–[22].

Bollella et al. [20] made a comparison between two plant peroxidases, cationic horseradish peroxidase (HRP) and anionic tobacco peroxidase (TOP) combined with a highly cationic osmium polymer [Os(4,4’-dimethyl-2,2’bipyradin)₆Poly(N-vinylimidazole)₁₀Cl]^{2+}/([Os(dmp)PVI])^{2+} to develop highly sensitive, stable and selective hydrogen peroxide biosensors. Furthermore, they carried out electrochemical experiments to investigate the influence of surface charge of the enzyme and the charge of the polymer on the efficiency of electron transfer between the enzyme and the wiring Os-redox polymer, see figure 2. The electron transfer rate decreased in HRP due to the repulsion between
the enzyme and the polymer, both positively charged, whereas with TOP there was an enhanced electron transfer due to attraction between the anionic enzyme and the cationic polymer [20,23].

![Figure 2. Schematic representation of HRP and TOP Os-polymer biosensors [20]](image)

Synthesis of the above mentioned Os-redox polymer biosensors allowed for accurate, cost-effective determination of hydrogen peroxide by electrochemical sensing based on electron transfer while saving time. Therefore, it was concluded that the wiring of redox enzymes with Os-polymer ensured an efficient electron transfer between the prosthetic group of enzyme and the electrode surface [20]. Such properties of Os-polymer is interesting for further studies in the biomedical field for innovative development of biosensors.

6. Redox flow battery applications

Redox flow batteries (RFBs) are attractive as stationary energy storage devices because of their rapid response times, high energy capacities and high storage efficiencies. Furthermore, they are advantageous because of their ability to provide specific power and energy requirement for a specific application. The storage capacity can be increased by adding electrolyte, so the incremental cost of each additional energy storage capacity unit is reduced than in other types of batteries [24].

It has been reported that the use of purely metal-based RFBs will most likely not be the energy-storage system of choice due to usage of toxic and harmful halogens and complexing agents, high-priced metal salts, corrosive acidic electrolytes and expensive ion-exchange membranes. In the VRFB systems, vanadium contributes about 30% to the overall cost of the battery. Therefore, the higher the price of vanadium, the higher the cost of the battery [25].

These redox flow battery limitations can be overcome by the development of environmentally sustainable, cost effective redox-active organic charge-storage materials, whose solubility and electrochemical properties can be adjusted by purposefully introducing substituents and functional groups instead of inorganic halogens. Aqueous all-organic RFB utilises low-cost membranes and sustainable, inexpensive organic-charge storage materials [25].

The development of osmium-based organic redox flow battery promises to be advantageous over other battery systems because; Organic redox flow batteries are environmentally friendly, low CAPEX is achievable because of the readily available osmium and easy synthesis of organic molecules, large capacity is achieved with electrolyte addition, and robust simple design. The organic batteries are modular and scalable because electrolytes can be replaced by new ones, more capacity with more electrolytes, and more power with more stacks. Here one has to choose whether or not power or stored energy is important, depending on the application. Low OPEX is achievable because of minimal maintenance, long life, and sustained performance [26,27].
The complexity of osmium compounds is a promising route for improvement of redox-active materials for use in RFBs. The use of Os-complexes promises the increased voltage efficiency and energy efficiency because it meets the requirements of a bipolar redox-active material. Generally, the synthesised organic osmium compounds should be able to meet the requirements for redox-active material, that is, it should offer properties such as:

- Feature two reversible redox reactions and can be used simultaneously as both cathode and as anode material in a symmetric RFB [29]–[31]
- Provide easier synthesis route [32]–[34]
- Eliminate the use of expensive ion-exchange membranes [35]–[37]
- Must have high electrochemical reversibility [25]
- Transfer more than one electrons during the redox process [25]
- Must have high cell voltage [25]
- Must have high solubility in the applied solvent [25]

In this current review, the summary of the chemistry of organic osmium compounds has been done and the characteristics mentioned above has been reviewed and reported. The first compounds to be discussed are the 2-(phenylazo) pyridine osmium complexes. The chemistry of 2-(phenylazo) pyridine osmium complexes have been studied and reported by Das et al.[33]. The OsBr$_2$ moiety was used as the reactive fragment because the Os-Br bonds disassociate easily even in mild condition, with two $\pi$-acid ligands, that is, 2-(phenylazo) pyridine (pap, 1) and triphenylphosphine (PPh$_3$) used to satisfy the remaining four coordination sites of Os in OsBr$_2$. The chemical synthesis of 2-(phenylazo) pyridine osmium complexes is explained in [33]. The synthesis allowed for the successive synthesis of [Os(PPh$_3$)$_2$(pap)Br$_2$] and [Os$^{II}$ (PPh$_3$)$_2$ (pap) (L)] ClO$_4$ (L= bidentate ligand). The electrochemical properties of these complexes were evaluated using cyclic voltammetry and the resulting voltammograms are shown in figure 3 for [Os (PPh$_3$)$_2$(pap) Br$_2$] in dichloromethane solution and [Os$^{II}$ (PPh$_3$)$_2$ (pap) (L)] ClO$_4$ in acetonitrile solution.

The [Os (PPh$_3$)$_2$(pap) Br$_2$] showed a reversible oxidative response at 0.49 V vs. SCE and two quasi-reversible reductive responses at -1.03 and -1.40 V vs. SCE. The oxidation is assigned to osmium (II)-osmium (III) oxidation. As part of the discussions, it was stated that the 2-(phenylazo)-pyridine ligand is known to accept successively two electrons in its lowest unoccupied molecular orbital. The cyclic voltammetry of [(PPh$_3$)$_2$ (pap) (L)] ClO$_4$ also showed reversible Os (II)-Os (III) oxidation at the
potential varying between 0.69 V and 1.01 V vs. SCE and two reductions below -0.9 V vs. SCE of the coordinated pap in acetonitrile solution, which has been used in RFBs as well [33]. These compounds are therefore excellent candidates for use as redox-active materials in RFBs and will be investigated further in the current project.

Another possible Os-complexes that promises to be useful in RFBs include the work that was done by Clayton et al.[38]. His work details the synthesis of arene-osmium complexes. The synthesis route of these complexes is shown in figure 4. The reactivity of Os-complexes were characterised using the NMR. However, the characterisation did not include electrochemistry. Since the synthesis of these compounds have been completed, it is worth a while to consider looking at cyclic voltammetry in order to evaluate the suitability of these complexes for use in RFBs. It was further stated that osmium has a shielding effect on the methylene protons adjacent to it. This might be the foundation for synthesis of a bipolar organic Os redox-active material to be used in RFBs [38].

![Figure 4. Schematic presentation of synthetic methods for dimeric η⁶-p-cymene Os (II) complexes[38]](image)

Another interesting Os (III) complex bearing two (carbene) borate ligands was synthesised by Chen et al.[32] building from the work done by Jia et al.[39]. The synthesis was performed by first reacting LiPhB(MeIm)₃ with [Os(COD)Cl₂]ₙ, of which no observed reaction took place after 1 day at temperatures between -20 and 60°C. In the second attempt, (Bu₄N)₂OsCl₆ was used as a starting material leading to formation of a purple solution. The resulting solution was purified and recrystallized to give a pure crystalline sample of [PhB(ImMe)₃]₂Os(OTf) (1b). The synthesis scheme is shown in figure 5 [32].

![Figure 5. Synthesis route of [PhB(ImMe)₃]₂Os(OTf) (1b) [32]](image)

It was reported that during the formation of compound (1b), the starting Os (II) was oxidised to Os (III). The complex was stable in solid and solution state. This is one of the important factors that enhance the performance of the battery. Therefore, this compound is one of the potential compounds to be considered for use in RFBs as the stability determines the life-time of the battery. Furthermore, it was reported that no decomposition was observed after standing in air for three months [32]. Further tests were carried out using cyclic voltammetry to investigate the electrochemical properties of
[PhB(MeIm)$_3$]$_2$Ru(OTf) (1a) and [PhB(MeIm)$_3$]$_2$Os(OTf) (1b) in MeCN/0.1 M NBu$_4$PF$_6$, glassy carbon electrode, scan rate 100 mV/s. The results showed two reversible redox waves, as shown in figure 6.

A reversible wave with $E_{1/2}$ value at 0.35 V vs $\text{Fe}^{2+}/\text{Fe}^3$ couple was attributed to the Os$^{III}$/Os$^{IV}$ couple. Another reversible wave was observed at -0.86 V and attributed to Os$^{II}$/Os$^{III}$ couple. The reversible redox waves indicated the strong donating nature of the tris-(N-heterocyclic carbene) borate ligand. This means [PhB(ImMe)$_3$]$_2$Os(OTf) compound is one of the potential for use in the RFB applications, which will take into advantage its electrochemical properties and easy synthesis routes [32].

![Cyclic voltammograms of [PhB(MeIm)$_3$]$_2$Ru(OTf) (1a) and [PhB(MeIm)$_3$]$_2$Os(OTf) (1b) [32]](image)

Figure 6. Cyclic voltammograms of [PhB(MeIm)$_3$]$_2$Ru(OTf) (1a) and [PhB(MeIm)$_3$]$_2$Os(OTf) (1b) [32]

7. Conclusions and future outlook

Over the past few years, there has been an interest in osmium for use in various applications and the initial research results suggest that it could find future application in complexes used in biosensors, biofuels and organometallic drugs for treating cancer. The establishment of easy and safe synthesis routes for Os compounds will also place a demand on osmium for use in redox flow batteries. The entry barriers to new entrants in such advanced applications, however, appears to be high, requiring access to precursor materials, strong collaborative research partnerships with universities, potential end-users, and sustainable long-term research funding.

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