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Review

Evaluation of anodic materials in electrocatalytic oxidative desulfurization

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SUMMARY

Electrochemical oxidative desulfurization is a highly attractive strategy for achieving low sulfur content in fuel oils. Compared with current hydrodesulfurization methods, electrochemical oxidative desulfurization offers relatively mild operating conditions, minimal waste generation, and electrode tunability. Despite the growth in interest, information about electrode materials and their performance for electrochemical oxidative desulfurization is scattered without an organized comparison. This review highlights the different materials that have been used for electrochemical oxidative desulfurization and compares their performance and electrochemical properties, with a focus on mechanistic insights that control activity. A wide range of electrode materials are compared and discussed, with a particular emphasis on noble metal, carbon, and metal oxide electrocatalysts. Directions for continued study are identified and standardizations for testing conditions are suggested.

INTRODUCTION

Crude oil and natural gas are made up of varying hydrocarbon species and naturally contain heteroatom impurities such as water, sulfur compounds, oxygen, nitrogen, carbon dioxide, and trace metals.[1] Sulfur-containing compounds in crude oil are particularly undesirable because they lead to the formation of the hazardous side product sulfur dioxide, which contributes to acid rain and can cause corrosion of catalytic convertors in car engines as fuel is combusted. As such, there are global regulations on the amount of sulfur that can be present in commercially available petroleum. Under the Clean Air Act Amendments of 1990, the United States Environmental Protection Agency set increasingly strict federal limits for sulfur content in fuel oils, with a most recent maximum of 10 ppm as of 2017.[2] The current leading industrial method of removing these sulfur-containing compounds is thermal hydrodesulfurization (HDS), which involves hydrogenation under high temperature (300°C–400°C) and pressure (30–130 atm) conditions while passing through a catalyst bed, typically molybdenum and/or cobalt based.[3] The overall chemical process with a sample sulfur impurity is shown in Figure 1.

Although the process of sulfur removal has been modified over decades to increase the efficiency of the process, HDS still has many shortcomings that have yet to be solved. The reaction conditions demand a high energy input, which is undesirable for both cost and environmental considerations. Additionally, the high-temperature conditions result in the degradation of oil components that produce unfavorable side products, resulting in a lower octane rating for the diesel.[4] One of the major byproducts of this reaction is H_2S, which has adverse effects on human health,[5] so additional processing is necessary for removal. Additionally, HDS has poor selectivity for

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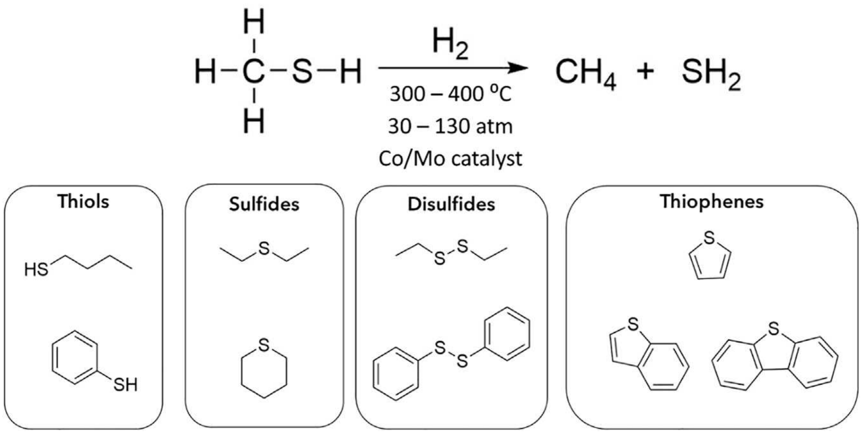


Figure 1. General chemical transformation of sulfur-containing compounds via HDS
Some examples of different classes of sulfur impurities found in unprocessed oil are depicted.

certain sulfur-containing impurities. In particular, polycyclic thiophenes such as dibenzothiophene (DBT) and derivatives do not interact well with the HDS catalyst surface due to steric bulk around the sulfur moiety. Figure 1 shows some representative structures of organosulfur compounds commonly found in raw petroleum.

Sulfur content restrictions continue to grow more stringent, and, due to the inability to effectively remove all types of organosulfur compounds, there is an inherent limit to how much desulfurization HDS can achieve on an industrial scale.[6] While laboratories have been able to demonstrate impressive catalytic activity for HDS in a laboratory setting,[7] the catalysts are often not practical for use on a large scale due to expense and instability. This suggests a necessary shift away from HDS for desulfurization of crude oils to more sustainable and selective methods such as adsorptive, biological, and oxidative desulfurization.

Adsorptive desulfurization involves physical abstraction of the target compounds from oil by selective binding to the sulfur moiety, frequently utilizing metal-organic framework structures,[8] zeolites,[9] or high-surface-area metal oxides[10] to increase the degree of cohesion. Adsorption requires a physical interaction with the substrate, which can be difficult with sterically bulky molecules such as DBT. Although not highly effective for desulfurization by itself, adsorptive desulfurization is sometimes employed in conjunction with other techniques that can better target all organosulfur molecules, as a secondary method of removal.[11] Sulfur-containing organic compounds can also be converted to elemental sulfur or sulfate by light autotrophic bacteria,[12] which have also served as inspiration for artificial, biomimetic desulfurization.[13] This can occur with or without the presence of oxygen. Under anaerobic conditions, sulfur-containing species are reduced and form H_2S as a byproduct, which would require the same processing as HDS.[14] This additional step, along with the difficulty of maintaining an oxygen-free environment, has led to a focus on aerobic biodesulfurization. With oxygen present, direct oxidation takes place and the sulfur within the compound is well targeted.[15] This leads us to one of the more promising routes to desulfurization: oxidative desulfurization (ODS).

ODS is a process by which sulfur species are oxidized and then extracted from oil by leveraging the increase in polarity of the oxidized sulfur relative to the environment.[16,17] ODS has demonstrated the capacity to reduce sulfur content in oil systems to extremely low levels, making it a particularly promising alternative to

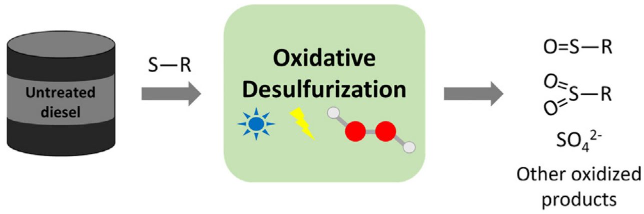


Figure 2. Overview of oxidative desulfurization
An overview of ODS of sulfur-containing compounds in raw oil to oxidized products via different methods.

HDS.[18,19] It is also highly tunable, as there are many factors that can affect the outcome of the reaction, such as catalyst choice, operating conditions, and the class of liquid fuel used.[20] Oxidation can be facilitated in several different ways[21]: by introducing a chemical oxidant such as H_2O_2,[22,23] photochemical transformation with light,[24,25] or through the application of an external voltage to an electrochemical system containing the target molecules. The overall process of ODS using each of these methods is outlined in Figure 2.

H_2O_2 is a highly potent oxidant, is readily available in large quantities, and water is the only major byproduct, making it the most common oxidizing agent used in ODS. The major drawback of this method is that H_2O_2 is not regenerated over the course of the reaction, leading to a constant need for more to be added throughout ODS. The mass of H_2O_2 required for total sulfur oxidation would be too great to make it a viable industrial process, even assuming stoichiometric efficiency.[26] Instead, H_2O_2 is often utilized as a co-oxidant alongside a heterogeneous thermal catalyst. In organic catalysis, the co-oxidant operates as a regenerator of the primary oxidation agent, as commonly seen in alcohol oxidation schemes, although it may participate in low levels of direct oxidation as well.[27] Photochemical oxidation can happen catalytically, with TiO_2-based materials common as semiconducting photocatalysts, or through the use of a molecular photosensitizer.[28,29] Photochemical ODS benefits from an ability to operate at room temperature and pressure, along with a higher selectivity for molecules that HDS does not target. However, it typically requires long periods of irradiation to achieve total sulfur removal, and most of the photocatalysts active for desulfurization can only operate under high-energy UV light.[30]

Electrochemical ODS (EODS) is a method that can operate under comparatively mild conditions, produces little waste, and can be easily tuned for specific applications. EODS can target specific molecules in an oil sample or operate under different electrolytic (solvent, salt, acidic/basic) conditions depending on what kind of organosulfur compounds are present in the fuel being processed.[31] There have been many examples of EODS systems that can achieve high levels of desulfurization (up to 100%)[32,33] and investigations into the effect of electrolyte and reaction conditions that affect this performance.[34] In this review, we survey the existing body of literature for electrochemically facilitated ODS reactions and look deeper into how the working electrode used in each case influences the reaction. Selectivity for certain oxidation products by the chosen electrocatalyst has been previously overlooked, so this comparison of many systems provides key insight to the mechanism of ODS.

BACKGROUND AND METRICS FOR EODS

There are several parameters that are typically reported in desulfurization studies and can be used as metrics for the overall effectiveness of an EODS catalyst. One clear measure of an effective catalytic system is the reported sulfur removal, which is the amount of sulfur converted from its original state to a more polar, oxidized form. Some studies follow the oxidation with an extraction step and report the sulfur content before and after processing. For ease of comparison across techniques, we will be assuming that 100% of the oxidized product would be successfully extracted, making the sulfur conversion and the sulfur removal effectively the same value. The Faradaic efficiency (FE) measures, out of all of the electrons passed during electrolysis, how many go toward product generation. A low FE is indicative of energy loss within the electrochemical system, whether it is from the presence of a competitive reaction, the formation of unintended side products, or the generation of heat. An ideal EODS catalyst will have a high FE, allowing for lower energy usage to facilitate complete sulfur removal, which is critical if this process is to be scaled up for industrial use. Activation energy (E_a) is another measure of a catalyst's performance. A lower energy barrier is favorable for reaction optimization since it is associated with faster kinetics and requires less energy input to facilitate product formation. An effective catalyst will significantly lower the activation energy of a reaction coordinate. In addition to these quantitative metrics, the electrolyte chosen is a parameter that must be considered, since electrolyte components (e.g., water or salt) can actively participate in the electrochemical reaction. A final metric for EODS is the type of product formed, since the selectivity of a catalyst is of great interest in electrochemical experimental design.

To fully understand the performance of an anode as a catalyst for EODS, we must establish a general mechanism of electrocatalysis, then a specific mechanism for EODS. There are two fundamental steps involved in electrocatalysis: mass transport and electron transfer.[35] First, the molecule to be reduced or oxidized must travel through the bulk solution to the electrode surface, which can happen via diffusion, migration, or convection. At the interface of the electrode and the solution, an electrical double layer is formed. This region consists of an inner coating of solvent, ions, and molecules that are adsorbed to the electrode, followed by a Helmholtz layer where ions only experience electrostatic interactions with the electrode, and finally a diffuse layer of ions that extends several hundred angstroms into the bulk solution. In the case of EODS, the anode is where the electron transfer takes place between the electrode and the molecule and is the site of electrocatalysis. The choice of anodic material is, then, intrinsically linked to the mechanism of oxidation. Oxidation of the sulfur impurity can take place through either direct or indirect catalysis (Figure 3).

Direct catalysis involves an electron transfer from a sulfur-containing compound to the anode, leaving an active cationic species that can then react further. Indirect catalysis occurs when a species other than the organosulfur is oxidized, and then mediates the desulfurization oxidation. We use this distinction to categorize EODS catalysts used in each study, allowing us to compare the mechanism facilitated by different electrode types.

Another key element to understanding the EODS mechanism is the role that the electrolyte plays during electrochemical processing. The majority of studies in this field contain some amount of water in the electrolyte used for EODS, and water is commonly identified as the source of oxygen when forming oxygenated products. Méndez-Albores and coworkers investigated the role that water plays in the catalytic process of EODS and found that the mechanism of oxidation for DBT was different depending on the concentration of water present in their electrolyte, as shown in Scheme 1.[36]

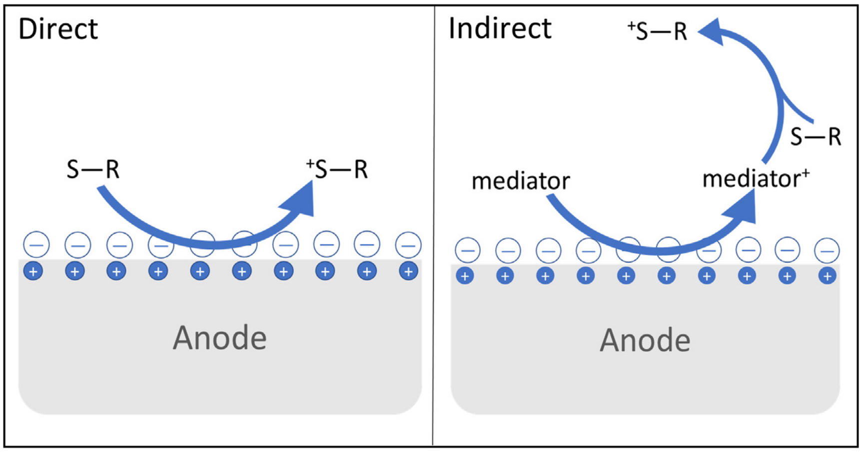


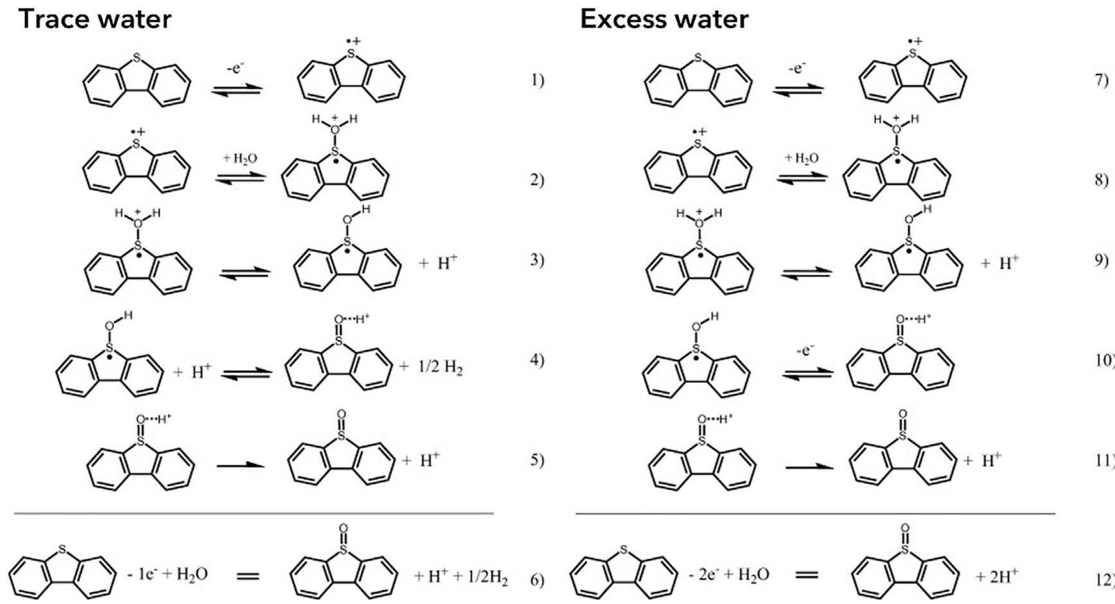
Figure 3. Mechanisms for direct and indirect oxidation
Diagram showing the mechanism for direct and indirect oxidation of a sulfur-containing compound in an electrocatalytic system.

As a primary step, DBT is oxidized to a radical cation, a step attributed to direct electron transfer at the electrode surface. Then, water is bound to the positively charged sulfur, existing as a cationic species before the elimination of a hydrogen atom to produce H^+ and an uncharged radical species. A change in reaction stoichiometry between low- and high-water-content systems (one electron at trace water levels and two electrons in excess water) is then proposed, explained by the higher concentration of water greatly increasing the rate of reaction for line 8 of Scheme 1. The intermediate, being rapidly formed at the electrode surface, does not have enough time to diffuse away from the electrode surface at high water concentrations. This leads to the species being directly oxidized at the interface rather than undergoing a redox reaction with the previously generated proton. If the applied potential is sufficiently large (2.29 V vs. SCE), DBT sulfoxide will oxidize to form DBT sulfone irreversibly. Alternate pathways for EODS have also been proposed, which depend on the electrode material and water content, and these will be explored more in depth later in this review. The type of electrode affects the interfacial interaction with water in addition to the organosulfur compounds, so it could lead to a difference in the overall mechanism.

The presence of water also leads to a possible side reaction: the oxygen evolution reaction (OER), which has a standard redox potential of 1.23 V as shown in Equation 1.[37]

$$2\,H_2O_{(l)} \leftrightarrow 4\,H^+ + O_{2(g)} + 4\,e^- \quad E^0 = +1.23\text{ V} \qquad \text{(Equation 1)}$$

This overlaps with the typical potential range applied for EODS (1.0–2.0 V), so there can be some loss of energy to water oxidation rather than the intended reaction. We recently explored the catalytic behavior of several materials for EODS and there was a clear difference in the activity after the addition of 2 M water.[38] In some cases (i.e., group 10 metals), there was a loss of FE due to the competitive OER taking place, while the FE was promoted for gold (Au) and glassy carbon, possibly by providing another route to oxidation. In fact, the mechanism of oxidation was certainly affected by the addition of water, seen by the inclusion of a sulfoxide product for every material that was previously not formed. Later in this review, we will discuss each anode in further detail, but this direct comparison shows how water can affect EODS in very different ways depending on the working electrode used.



Scheme 1. The mechanism of oxidation of dibenzothiophene

The mechanisms of oxidation to sulfoxide are shown in the presence of trace water (1–6) and excess water (7–12).[34]

PLATINUM ANODES FOR EODS

In the realm of electrocatalysis, platinum (Pt) has been shown to effectively facilitate a myriad of small-molecule transformations, including methanol oxidation,[39] oxygen reduction,[40] and carbon monoxide oxidation.[41] Unsurprisingly, it is also one of the most used materials in EODS due to its high catalytic activity. Most of the studies that utilize Pt for EODS report highly efficient reactions, with 80%–100% conversion of the sulfur-containing substrate to an oxidized product. Pt was used as an anode in many early fundamental studies of EODS. A report from Cottrell and Mann[42] used an electrolyte of acetonitrile and sodium perchlorate and reported the oxidation of aliphatic sulfides at a Pt surface, which produced the corresponding sulfonate. However, upon the addition of as little as 1% water by volume, the sulfide is instead completely oxidized to the sulfone species, suggesting that catalysis is highly sensitive to the composition of the electrolytic environment. They observed a much larger current onset at a lower potential after the addition of water, requiring the bulk electrolysis to be carried out at a potential of 1.2 V rather than the 1.4 V used in anhydrous media. This indicates how the solvent window is shortened by the presence of water using a Pt electrode. Bontempelli et al. investigated a highly similar anhydrous system, also using a Pt wire in a rigorously dried electrolyte of sodium perchlorate in acetonitrile.[43] Instead of an aliphatic sulfide they used DBT, and, upon oxidation, a dimerized sulfonium salt was formed. This is likely because, in DBT, the sulfur is part of an aromatic system, allowing for stabilization of the sulfonium ion long enough for recombination with another oxidized DBT radical species. In fact, Cottrell and Mann suggest that oxidation of aliphatic sulfides also forms a sulfonium intermediate as "the immediate major product" of the oxidized sulfide species, but, without the delocalization of charge, it reacts rapidly to form the sulfonate.[40] The source of oxygen for the formation of sulfonate is attributed to the electrolytic perchlorate anion, which can disproportionate to a small degree to form H_2O and Cl_2O_7. This is the most plausible explanation as the addition of even 1% volume of water shifts the product generation entirely to sulfone. It is also consistent with the findings of Bontempelli, as it would be more favorable for DBT sulfonium ions to react with one another than with trace water in the electrolyte. It is probable that, if water were added to Bontempelli's electrolyte, the major product would be DBT sulfone instead of the dimerized sulfonium salt. However, the high activity of Pt for catalysis of other reactions such as water oxidation leads to a Faradaic loss, which must be considered in the desulfurization of a complex system such as unprocessed oil, which contains many components other than the target molecule.

We recently studied the catalytic performance of Pt in the presence of water using DBT as a model substrate.[36] The FE measured for the oxidation of DBT in anhydrous conditions was 27.4% but dropped to 21.5% upon the addition of 2 M H_2O, demonstrating the energy loss to water oxidation. Oxidation of DBT on a Pt electrode was observed at approximately 1.6 V vs. the standard hydrogen electrode (SHE), while water oxidation occurs at 1.23 V vs. SHE. This means that the applied potential to oxidize DBT also corresponds to a larger overpotential for OER, which will occur preferentially on a good OER electrocatalyst such as Pt.[44] It also was observed that, in the absence of water, the only product formed was DBT dimer, but a mixture of dimer and sulfoxide were produced in 2 M H_2O, which was consistent with the results of Cottrell and Mann.[40] A study by Gong et al. also addresses the competition between ODS and water oxidation during the electrolysis of a solution containing bauxite in a water-based electrolyte.[45] Bauxite is a rock rich in aluminum,[46] and, during its processing, a sulfur-containing phase (FeS_2) is transformed to sulfates, which cause corrosion of equipment, leading to a need for sulfur removal prior to aluminum extraction. The study used a Pt sheet to oxidize the reaction mixture while varying bauxite concentration and stirring speed to examine the relationship between oxygen evolution and desulfurization. It was determined that the oxidation of FeS_2 to sulfate had an optimal recorded sulfur removal of around 80%, while the FE had a maximum of roughly 50%, which is expected due to the current contributing to water electrolysis.

Another consideration for using a Pt anode for EODS is the possibility of surface buildup over the course of the reaction. Barsch et al. investigated the oxidation of three thiophenes to their polymerized form, leveraging the interactions of the monomers at the surface of the Pt to form polymer films that can then be selectively functionalized.[47] The study exhibited how water content can be leveraged to selectively form specific products (e.g., thiophene can be oxidized through polymerization, then select polythiophene monomers can be oxidized to sulfone). While Pt can be used to intentionally polymerize sulfur-containing compounds, unintentional buildup on the surface can lead to decreased catalytic activity over time. This obstacle was addressed by Hourani in a study using square-wave potentiometry to oxidize thiophene rather than traditional controlled potential electrolysis.[32] The advantage of this technique is that the surface of the Pt electrode is periodically cleaned, preventing any accumulation of polythiophene on the anode. The thiophene was instead primarily oxidized to a sulfate and total conversion reached 100%, showing the importance of an active Pt electrode. Table 1 shows a comparison of studies using Pt for sulfur oxidation, their reaction conditions, and the resulting products and any reported yields.

Overall, Pt displays an impressive capacity for EODS, but the competitive OER reaction and the surface effects narrow the conditions in which it can be effectively utilized. Additionally, Pt is a precious metal and is not a sustainable choice for a catalyst operating on an industrial scale.

Other transition metal anodes

Although not used as extensively as Pt or carbon due to a lack of activity and/or selectivity, EODS has been catalyzed using other transition metals (Table 2). One

Table 1. Comparison of ODS reactions catalyzed by a platinum electrode

Substrate	Electrolyte	Product	Sulfur removal (%)	E_a (kJ/mol)	FE (%)	Reference
Bauxite (FeS_2)	NaOH	sulfate, iron oxyhydroxide	Up to 80	10–30	~50	Gong et al.[45]
Sulfides	0.1 M $NaClO_4$ in ACN	sulfonate (anhydrous), sulfone (trace water)	–	–	–	Cottrell and Mann[42]
DBT	0.1 M $NaClO_4$ in ACN	dimerized sulfonium salt	–	–	–	Bontempelli et al.[43]
Thiophene	H_2SO_4	sulfate	100	–	–	Hourani[32]
Thiophene, 3-MT, 2,2′-BT	Fluka prum	polythiophene	–	–	–	Barsch and Beck[47]
DBT	0.1 M NH_4PF_6 in ACN	DBT dimer (anhydrous), sulfoxide (2 M H_2O)	43.6	16.1	27.4 (anhydrous), 21.5 (2 M H_2O)	Kompanijec and Swierk[38]

metal that is vital to the realm of catalysis is palladium (Pd), which is expected to have similar catalytic behavior to Pt due to their similar electronic properties. This was the focus of a study by Márquez-Montes et al., who used a Pd-coated glassy carbon electrode to probe the kinetics of sulfite oxidation and compare it with Pt, the current industry standard for sulfite electrooxidation.[48] They found that Pd displays good catalytic activity, with comparable results with Pt at a pH of 8.5. They also postulate that, at low potentials, sulfite is oxidized through an adsorption mechanism, while being directly oxidized on the Pd surface at high potentials, supported by the presence of a bisulfite radical intermediate that forms upon adsorption. It is not readily apparent how electrochemical adsorption differs from a direct oxidation, but it appears that it is defined by the authors as a stronger chemical interaction than that of a typical electron transfer step. The reported activation energies for sulfite oxidation to sulfate range from 16 to 18 kJ/mol depending on the pH used. This is in good agreement with the activation energy we report for the oxidation of DBT using a Pd electrode in hydrous conditions (18.3 kJ/mol), which was also found to exhibit similar catalytic properties to Pt.36. Although there are numerous similarities between Pd and Pt, it is important to note that Pd is even less abundant than Pt and is prone to catalyst poisoning.[55]

A 1987 study by Bravo et al. looked at the oxidation of 2,5-dihydroxythiophenol (DHT) using an Au electrode, with a specific focus on the binding method between electrode and DHT and aimed to compare the DHT oxidation mechanism on both electrodes.[49] Through cyclic voltammetry and differential coulometry, they found that the mode of binding for DHT was through the SH group on both Au and Pt and that there were similar packing densities measured on each electrode. However, they determined that there were differences in the cyclic voltammetry oxidation

Table 2. Comparison of ODS reactions catalyzed by non-platinum transition metals

Electrode	Substrate	Electrolyte	Product	Sulfur removal (%)	E_a (kJ/mol)	FE (%)	Reference
Pd	sulfites	0.5 M sulfate in water	sulfate	–	16–18	–	Márquez-Montes et al.[48]
Pd	DBT	0.1 M NH_4PF_6 in ACN	Dimer, sulfoxide	38.1	18.3	30.6	Kompanijec and Swierk[38]
Au	DHT	H_2SO_4	not specified	–	–	–	Bravo et al.[49]
Ir	DHT, DHMBM, PFT	H_2SO_4	not specified	–	–	–	Bothwell and Soriaga[50]
Au	DBT	0.1 M NH_4PF_6 in ACN	dimer, sulfoxide	40.0	8.63	87.9	Kompanijec and Swierk[38]
Fe	raw oil (thiols)	NaOH	disulfides/sulfones	91.3	–	–	Li et al.[51]
Cu	crude diesel	NaOH	SO_4^{2-}, sulfoxides, sulfones	65.3	–	–	Tavan et al.[52]
Cu	crude diesel/BT	NaOH	sulfone	65	4.08	–	Tavan et al.[53]
Ni	DBT	0.1 M NH_4PF_6 in ACN	dimer, sulfoxide	39	11.5	28.6	Kompanijec and Swierk[38]
Ni	Coal	1 M NaOH	not specified	~60	–	–	Zhou et al.[54]

peak broadness between the metals, which they propose is caused by a difference in the level of interaction between the rest of the molecule and the electrode; there is evidence that the entire molecule is completely immobilized on a Pt surface,[56] which leads to heightened chemical interactions at the electrode interface, while Au binds strictly through the SH moiety. A later study extended this work to include iridium (Ir) as an anodic material, as well as exploring the oxidation of two additional thiophenols. When using an Ir electrode, there was less DHT loading compared with Au and Pt, which the authors propose was due to a bidentate binding pattern enabled by a higher affinity for the aromatic ring.[57] Similar binding patterns to DHT were observed for 2,5-dihydroxy-4-methylbenzylmercaptan (DHMBM) and pentafluorothiophenol (PFT).[50] The lower packing density on Ir means that there is a weaker interaction with the thiol group than Pt or Au. However, despite the difference in binding method, it was found that Ir performed similarly to Pt during anodic oxidation. They were both active for the oxidation of DHMBM and DHT but were not effective as PFT oxidation catalysts until after a reductive current was applied. PFT has different reactivity from DHT and DHMBM because the fluorine groups on the central ring withdraw electrons, resulting in only the SH group binding to the electrode surface. This reduces the substrate-metal interactions in Pt and removes the second binding site entirely in Ir. It was proposed that reduction led to the formation of a sulfur layer at the electrode surface, which then was easily oxidized. Au displayed different electrocatalytic behavior than Pt and Ir. It was observed that, compared with Pt or Ir, reductive desulfurization was not effective when using an Au electrode. However, performance on Au was comparable with Pt and Ir for the oxidation of DHT and DHMBM. Additionally, Au was able to directly oxidize PFT without the need of an initial reduction step, with a sulfonate derivative of pentafluorobenzene as the proposed product. In the context of ODS, this suggests that Au or Ir can compete with Pt as possible anodic materials, but all three metals still face a major issue of cost that using precious metal catalysis presents.

Our previous study also explored the difference in catalytic activity between Au and Pt.[36] There was a marked difference between the selectivity for the sulfoxide (DBTO) upon oxidation of DBT, with Au converting 25.6% of DBT to DBTO out of 40% oxidized product, and Pt produced roughly half of that amount of DBTO while achieving an overall desulfurization of 43.6%. Au also had a much higher FE, reaching almost 90% FE in the presence of 2 M H_2O, indicating that there was very little energy lost to water oxidation. A follow-up study explored DBT oxidation on Au over time, demonstrating that the highest rate of catalysis occurs within the first hour of electrolysis, forming DBTO and DBT dimer in similar proportions, then declines in DBTO production over time. The FE also decreases over the course of bulk electrolysis, but it is hypothesized that the balance in product is lost to oligomerization of DBT beyond the dimer. This would lead to product buildup on the electrode surface, which deactivates catalysis. This supports the hypothesis from Bravo et al. that Au operates as a direct catalyst, binding to the sulfur moiety of the target molecule and experiencing a similar catalytic poisoning to Pt over extended periods of electrolysis.[48]

Iron (Fe) is a popular choice as an electrode for large-scale electrolysis due to the low cost and its access to multiple oxidation states (Fe^0, Fe^{2+}, Fe^{3+}).[58] However, at sufficiently large overpotentials (such as those required to oxidize sulfur-containing compounds) Fe electrodes tend to undergo surface morphological changes and exhibit a lack of long-term stability.[59] This would typically exclude Fe from the scope of practical EODS electrocatalysts, but its instability was actually leveraged by Li et al. and promoted a mechanism to enhance desulfurization of kerosene beyond what was achieved with a graphite sheet under the same conditions.[51] They observed that the Fe sheet was initially oxidized upon reaction with an NaOH electrolyte to form FeO_4^{2-}, which then mediated an oxidation of long-chain thiols in the raw oil to disulfides and eventually sulfones, which were extracted from the raw oil. This strategy resulted in a reduction of sulfur content from 180 to 15.7 ppm, whereas the same process catalyzed by graphite only reduced the content to 116.4 ppm. It is unclear whether this indirect method of EODS would be as effective when expanded to a wider scope of sulfur-containing compounds, such as refractory, aromatic species targeted by other catalysts (e.g., DBT).

Copper (Cu) was utilized as a working electrode by Tavan et al. who aimed to optimize desulfurization by changing sets of variables such as electrolyte concentration, stirring speed, and concentration of oil.[52] They performed electrolysis on crude oil mixed into a NaOH electrolyte and found that the sulfur content was reduced from 5,750 to 2,016 ppm, a reduction of 65%. The major products detected were a mixture of sulfate ions, sulfones, and sulfoxides. The authors state that Cu was chosen as the anode "because of [its] easy operation and mild process conditions," so it appears that the catalytic activity or selectivity was not a major factor in the experimental design. A second study by the same group looked at modeling a highly similar system to gain more insight into the kinetics of the EODS reaction. They simulated the electrolysis of crude diesel in NaOH with added benzothiophene (BT), leading to an overall sulfur removal of 65% after 8 min under optimal conditions (extraction with DMSO at 1–4 bar and a solvent flow rate of 80 kmol/h).[53] The E_a for BT oxidation was determined to be 4.08 kJ/mol, although it remains difficult to assess the accuracy of that value, since it was assumed that only the sulfone was produced, which is not in agreement with the group's previous findings that a Cu-catalyzed EODS system forms a mixture of products. Additionally, given that the sulfur removal plateaued at roughly 65%, it seems unlikely that Cu-catalyzed oxidation would have a lower barrier than the reported values for a material such as Pt, which has a higher capacity for sulfur removal.

Nickel (Ni) is a common catalyst for organic transformations, and has been used in electrocatalytic applications, primarily as an anode for electroplating other metals.[60] Because of its catalytic properties and similar electronic characteristics to Pt, it was investigated as a working electrode for EODS.[38] For the oxidation of DBT, it was found that there was an FE of 28.5%, and no major change in this value was measured after the addition of 2 M H_2O. The major product upon electrolysis was DBT dimer, with a low percentage (16.5%) of DBT instead being oxidized to DBTO. However, electrolysis was not possible once water was added to the system because the electrode surface, in a similar manner to Fe, became unstable due to water oxidation. Ni was also used as the working electrode in a cell designed by Zhou et al. capable of achieving high temperatures and pressures.[54] They aimed to couple desulfurization of coal with electrochemical water splitting, as the intense conditions stabilize the OH intermediate and help facilitate desulfurization. They were able to achieve a desulfurization of roughly 60%, but it required a temperature of over 200°C and a pressure of 2.1 MPa.

Carbon-based anodes

In recent years, materials derived from carbon, which tend to be stable and low cost, have emerged as some of the most common electrode materials in a variety of applications, including pharmaceutical analysis,[61] perovskite solar cells,[62] and neural electro-sensing.[63] Due to these favorable qualities, carbon-based electrodes have also been investigated for EODS, especially with the goal of scaling up to an industrial level in mind. There have been several studies that utilize carbon-based electrodes for systems that mimic a raw oil to gain an idea of maximum practical sulfur removal. Li et al. investigated the effects of emulsifying diesel on the desulfurization rate, using a graphite sheet as an anode.[64] They reported that their system, with an original diesel sulfur content of 624.4 μg/g, had a sulfur removal of 98.71%, and a measured E_a of 9.1826 kJ/mol without and 6.9783 kJ/mol with emulsifying. These measurements suggest that, under a set of optimized conditions (i.e., temperature, stirring, electrolyte concentration, and sufficient current), a simple graphite sheet can exhibit high activity for EODS. However, the Li study does not specify the type of sulfur-containing compounds that are present in the diesel, nor the products they form upon oxidation, so it is difficult to use their findings to directly compare with another system. The reactivity can be surmised, however, by looking at a closely related electrochemical experiment by Tang et al. In two separate studies, a graphite working electrode was used to facilitate the desulfurization of kerosene containing sulfides[65] and condensate gasoline that included organic sulfides.[66] In both cases, the percentage removal of the sulfur-containing components reached high levels, with 92.67% removed from the kerosene and ''almost all'' from the condensate gasoline. The products that were formed from the oxidation of the sulfides were a mixture of the corresponding sulfoxides and sulfones. Due to the high degree of similarity of the systems, it can be surmised that these same products were formed by the Li study as well. However, it is unclear whether the glassy carbon surface itself participates in heterogeneous catalysis as is seen in the case of Pt or other transition metals. In fact, the Tang group proposed that the oxidation of sulfides is facilitated by H_2O_2 that is formed by the oxidation of water within the electrolyte. This deviates from the mechanism suggested by Méndez-Albores, which attributes the oxidation of DBT to an electron transfer at the electrode surface, followed by a reaction with water.[36] Regardless of whether the organosulfur or water are oxidized at glassy carbon, it appears that the product selectivity is the same, and is further verified by the findings of Harandi et al.[67] They used a glassy carbon electrode to oxidize DBT in a 9:1 MeCN:water electrolyte, which also served as an extraction solvent. After applying a potential of 2.9 V for 5 h, DBT sulfone was formed, achieving nearly 100% desulfurization of the system after a liquid-liquid extraction.

Unlike Pt, it does not appear that buildup of oxidized products on the surface of a carbon electrode is a concern, even in the case of relatively slow diffusion from the interface in hydrated conditions. In particular, the polymerization of thiophenes that was observed by Barsch and Hourani[45,46] on a Pt electrode has not been reported in any EODS reaction catalyzed by a carbon-based material. This robust nature makes carbon an ideal electrocatalyst to study EODS in the context of a more complex environment. For instance, glassy carbon was used as an anode to oxidize sulfur-containing compounds in a deep eutectic solvent (DES) and analyze the effects of acidity on the electrolyte.[68] Hao et al. converted BT, DBT, and 4,6-dimethyldibenzothiophene (4,6-DMDBT) to a mixture of sulfoxides and sulfones and reached removal of up to 99%, although they attribute the catalytic activity to the presence of H_2O_2 in the DES. The proposed oxidation would take place in the bulk solution, away from the electrode interface, and would be impacted by the amino acid structures within the DES, as well as the acidity.

In addition to simple carbon materials such graphite and glassy carbon, a popular modified electrode in electrochemical studies is boron-doped diamond (BDD) due to its high conductivity and stability at high oxidizing potentials, even in aqueous conditions.[69] An EODS study utilized BDD to investigate the mechanism of oxidation for several thiophenes, i.e., DBT, 4-methyldibenzothiophene (4-MDBT) and

4,6-DMDBT, in the absence of a chemical oxidant such as H_2O_2.[33] Using linear sweep and cyclic voltammetry, along with chronoamperometric analysis at different water concentrations, Ornelas Dávila et al. determined that the sulfur-containing compounds were being oxidized both directly at the BDD surface through electron transfer (direct) as well as by interaction with radical oxygen species in the bulk solution being generated by simultaneous water oxidation (indirect). It is likely that BDD's heightened conductivity allows for a more rapid electron transfer step leading to interfacial oxidation of sulfur, whereas other carbon-based electrodes tend to only facilitate indirect oxidation. Despite this difference in mechanism, the product formation was still selective for sulfoxide and sulfone with all of the thiophenes tested. Although not an example EODS, BDD was also utilized in a unique approach to desulfurization, in which a reductive voltage was applied to an electrochemical cell containing coal and $NaBO_2$.[70] The $NaBO_2$ was transformed to $NaBH_4$ upon reduction, which then reacted with the sulfur contents of the coal to form Na_2S and Na_2S_x, leading to a maximum of 2.08 g sulfur removal and a desulfurization efficiency of 64.1%. The BDD electrode was key to this experiment due to its low capacity for the hydrogen evolution reaction, which is a competing reaction in the potential window required for $NaBO_2$ reduction to $NaBH_4$.[71]

When looking broadly at the catalog of carbon-based materials for EODS, a few common trends come to light. The most notable similarity is that the product formation heavily favors sulfoxides and sulfones, whether the target substrate is a sulfide, thiol, thiophene, or some related derivative. While Pt may show a tendency to form sulfate or sulfonate derivatives over other products more frequently, it is not consistent in the way that carbon-based materials are for forming sulfoxides and sulfones. This implies that carbon may be useful to selectively form these products over other possible pathways, and this is supported by some work done in electrosynthetic organic chemistry. Molecules that contain sulfoxide and sulfone components are of great interest due to their use in pharmaceuticals and fuel cell applications,[72,73] which has led to a demand for an optimized oxidation route. A recent report discussed the conditions needed to maximize the yield of sulfoxides and sulfones from the oxidation of different alkyl aryl sulfides, and they discovered that the sulfoxide was favorably formed under electrolysis with a graphite anode.[74] Even though this study is not in the context of desulfurization, it demonstrates the same product selectivity of carbon-based electrodes, which appear to oxidize through the addition of water to the structure, followed by a hydrogen elimination, as was proposed by Méndez-Albores.[36] Table 3 shows a comparison of experimental details for all carbon electrodes used in ODS discussed in this review.

Metal oxide anodes

Transition metal oxides have been used for electrochemical oxidation due to durability and adjustable electronic properties, generally in the context of energy storage (Table 4).[80] One class of metal oxides of high interest for catalysis is Fe oxides, due to being cheap, abundant, and available in a wide range of structures. They have also been investigated in recent years as photocatalytic materials and have shown promising results.[81] Recently, we tested an electrodeposited Fe oxide film as an EODS catalyst and it displayed high activity for DBT oxidation compared with Au (deposition substrate) at long timescales.[75] The FE reached over 80% at 24 h, while Au experienced a decline in FE from nearly 90% to roughly 40% during the same time frame. It was also observed that the Fe oxide film was highly active for conversion to DBTO (producing double that of Au), but it required a structural change before activity began. A morphological change from ϒ-FeOOH to ϒ-Fe_2O_3 was observed, indicating that EODS activity is dependent on the Fe oxide morphology.

Table 3. Comparison of ODS reactions catalyzed by a carbon-based electrode

Substrate	Electrolyte	Product	Sulfur removal (%)	E_a (kJ/mol)	FE (%)	Reference
DBT	$^tBuNH_4$ PF_6/$^tEtNH_4$ PF_6 in ACN	DBT sulfoxide/sulfone	–	–	–	Méndez-Albores et al.[36]
Sulfides	NaCl	sulfoxides/sulfones	92.67	–	–	Tang et al.[66]
DBT, 4-MDBT, 4,6-DMDBT	$NaNO_3$	sulfoxides/sulfones	97.5–99.2	–	–	Dávila et al.[33]
Diesel	10% acetic acid with NaCl mediator	not specified	98.71	6.98	–	Li et al.[51]
DBT	MeCN in water	DBT sulfone	~100	–	–	Harandi et al.[67]
Coal	NaOH	Na_2S/Na_2S_x	–	–	64.1	Shu et al.[70]
Thiols	10% H_2SO_4	sulfoxides/sulfones	–	–	–	Tang et al.[66]
DBT, BT, 4,6-DMDBT	L-proline/organic acid DES with H_2O_2	sulfoxides/sulfones	99	–	–	Hao et al.[68]

Cerium oxide (CeO_2) supported on carbon was used by Wang et al. to facilitate EODS with a maximum removal of 92% from a sample of gasoline with an initial sulfur content of 310 ppm.[76] They also electrolyzed three model organosulfur compounds (ethanethiol, ethyl thioether, and thiophene) to gain insight into the mechanism of oxidation taking place at the CeO_2 surface. They propose that, in the case of their electrocatalyst, an indirect oxidation of the organosulfur compounds took place via a mediator, as is commonly observed for other metal oxide electrodes.[82] This was supported by the observation that, after Ce^{3+} ions were introduced to the electrolyte, the overpotential required for desulfurization decreased, which implies that the catalysis occurs within the bulk solution rather than at the electrode surface. As is seen in other ODS schemes, the oxygen source is water contained in the electrolyte and the authors state that, upon oxidation, the sulfur compounds form sulfate ions and organic fragments. CeO_2 was also used by Du et al. to investigate the electrochemical desulfurization of diesel, but CeO_2 was incorporated into porous anodic aluminum oxide nanotubes (AAO-CeO_2).[77] FTIR spectroscopy, ion chromatography, and XRD indicated that, after 2 h of electrolysis, cerium and aluminum sulfates and sulfonic acid are formed with an overall sulfur removal of 75.2% for diesel. This indicates that the electrode surface is not fully inert over the course of electrolysis, with CeO_2 specifically being consumed. This does not lead to catalyst deactivation, however, since free Ce^{3+} ions in solution react with water to re-form CeO_2 on the anode. The authors confirm the proposed mechanism of oxidation in a follow-up study using model sulfur-containing compounds (BT, DBT, and 4,6-DMDBT).[78] The desulfurization efficiencies for these compounds using the AAO-CeO_2 catalyst ranged from 92.65% to 98.07%, with an inverse relationship between the steric bulk of the molecule and the measured desulfurization efficiency. Product formation was also dependent on the molecule, as BT was found to form a sulfone or sulfides upon oxidation, while DBT and 4,6-DMDBT were oxidized to sulfates and organic fragments. This lack of selectivity would make extraction of oxidation products more difficult in an industrial desulfurization setting. Other metal oxides were considered in a study that compared the oxidation of thiophene at electrodes with different overpotentials for oxidation.[79] They categorized electrodes into two categories: high oxidation power, which have a high EODS overpotential and indirectly catalyze oxidation, and low oxidation power, which have lower EODS overpotentials and directly interact with substrates to promote oxidation. Two materials previously discussed in this review were included in the material scope, with Pt as a low-oxidation-power and BDD as a high-oxidation-power electrode. Both assignments match with the methods of interaction between the sulfur-containing compounds and anode surface documented by other groups studying EODS. The other materials were a dimensionally stable anode (DSA) (a mixed ruthenium and Ir oxide supported by a titanium base, previously shown to oxidize organics)[83] and lead/lead oxide (Pb/PbO), categorized as low and high oxidation power anodes, respectively.

Table 4. Comparison of oxidative desulfurization reactions catalyzed by metal oxides

Electrode	Substrate	Electrolyte	Product	Sulfur removal (%)	E_a (kJ/mol)	FE (%)	Reference
$FeOOH/Fe_2O_3$	DBT	0.1 M NH_4PF_6 in ACN, 2 M H_2O	DBTO, dimer	94	18.6	90	Kompanijec et al.[75]
CeO_2/C	gasoline (ethanethiol, ethyl thioether, thiophene)	Ce(NO3)3	SO_4^{2-}, organic fragments	92	–	–	Wang et al.[76]
AAO-CeO_2	diesel	Ce(NO3)3	$CeSO_4$, $Al_2(SO_4)_3$, sulfonic acid	75.2	–	–	Du et al.[77]
AAO-CeO_2	BT, DBT, 4,6-DMDBT	Ce(NO3)3	BT: sulfone, sulfides DBT, 4,6-DMDBT: sulfates	92.65–98.07	–	–	Du et al.[78]
DSA: 30% RuO_2, 70% IrO_2	thiophene	H_2SO_4	Thyox, polythiophene	–	–	–	Mehri et al.[79]
Pb/PbO	thiophene	H_2SO_4	SO_4^{2-}, CO_2	–	–	–	Mehri et al.[79]

It was found that both low-oxidation-power electrodes selectively converted thiophene to a polar product with an added carbonyl and alcohol (Thyox), although DSA tended to form polythiophene at lower applied potentials, leading to a lower coulombic efficiency. The high-oxidation-power electrodes, in contrast, converted thiophene to Thyox, as well as facilitating "electrochemical mineralization," in which thiophene is degraded to compounds such as sulfate and carbon dioxide. The advantage of using a high-oxidation-power electrode such as BDD or Pb/PbO is that they have a high overpotential required for OER, which reduces the current that is consumed by the competing reaction and allows higher potentials to be applied to facilitate EODS. This study is a major step toward understanding the reactivity of sulfur-containing compounds during EODS and how the working electrode can significantly affect both the type of product formed and the efficiency of the sulfur conversion. It also displayed how metal oxides, under specific conditions, can mimic the catalytic behavior of more expensive materials, which would allow large-scale EODS costs to be driven down.

CONCLUSIONS AND OUTLOOKS

A variety of possible EODS anode materials have been demonstrated across many different studies, with some materials exhibiting high levels of sulfur removal and reported activation energies below 40 kJ/mol. The choice of working electrode influences the mechanism of oxidation and, therefore, the types of products formed. Pt electrodes can be highly effective for sulfur removal, but, due to their direct interaction with the target molecule at the active site, they are susceptible to deactivation over time due to product accumulation. Also, due to the high activity of Pt for water oxidation, any systems that contain water exhibit a decrease in FE because of water oxidation or must operate under lower overpotentials. Other transition metals lack the extensive library of studies that Pt and carbon have been used in, which makes it difficult to determine possible trends or draw direct comparisons. It appears that, out of the possible electrode materials for EODS, solid Fe is only capable of catalyzing EODS after "activation" through a reaction with electrolytic species, forming a homogeneous catalyst system. Cu was shown to facilitate only up to 65% desulfurization both in raw oil and after the addition of BT, with a reportedly low E_a (~4 kJ/mol), although there was no apparent selectivity for one type of product. Pd, Au, and Ir have all been shown to facilitate EODS to a similar extent as Pt. However, they suffer from the same issues of expense and scarcity and would not be suitable for any future large-scale applications. Carbon-based materials are much more inexpensive than Pt and have shown similar maximum desulfurization capacities given enough time to react. They generally form sulfone and sulfoxide derivatives of sulfur-containing compounds, likely after reaction with water or *in situ*-produced H_2O_2 from water

Table 5. Summary of advantages and disadvantages for each type of electrode used in EODS

Electrode material	Advantages	Disadvantages
Pt, Pd	high catalytic activity	surface deactivation, Faradaic loss to water oxidation, expensive
Ir, Au	high catalytic activity	expensive, not well-studied for EODS
Ni, Fe, Cu	inexpensive	lower sulfur removal, only suitable under specific conditions
Carbon-based	high sulfur removal, stability, selectivity for sulfoxides and sulfones	conductivity is low without modification (raises cost and complexity)
Metal oxides	ability to be modified for product selectivity, inexpensive	not well-studied for EODS

oxidation. The stability and ability for modification make this class of working electrodes one of the more promising for possible large-scale applications, whether as simple materials such as graphite or glassy carbon or a more sophisticated anode such as BDD. Metal oxides demonstrate how simple structural modifications can influence large changes in catalytic behavior. CeO_2 shows promise as an EODS catalyst both as a stand-alone electrode as well as incorporated within alumina oxide, with a desulfurization over 90% in cases of model sulfur compounds and roughly 75% in actual diesel. Metal oxides were also shown to have similar catalytic activity to previously established anodes, with DSA showing similar reactivity to Pt (both of which form a polar product) and Pb/PbO following a similar pathway as BDD (forming sulfate ions and organic fragments). This demonstrates how the material used as an anode can tune which products are formed at different applied potentials, and how less expensive materials have the capacity to rival the catalytic activity of their more expensive counterparts. Table 5 broadly summarizes the merits and limitations of each type of anode reported in the literature for EODS catalysis.

With all these works considered, there is still more to be done in the field of EODS before the intricacies of the electrode-compound interface are fully understood. However, it has already been shown that the anode choice can influence the oxidation product, and this selectivity would be greatly beneficial for industrial EODS. Also, the way that the working electrode interacts with electrolyte components (e.g., water or salts) can influence the course of the reaction. Of the materials tested, carbon-based species and metal oxides show the most long-term promise for practical applications and should be investigated further.

In this review, we make a concerted effort to use these standards to compare the results of different studies; however, there are many cases where key catalytic benchmarks are not included in the report. This leads to the conclusion that a standardization of analytical methods is needed in the EODS for more discernable patterns and comparisons to emerge. Future studies should focus on filling out the library of EODS catalysts, as there are many unexplored electrolytic systems, but should only choose a novel anode material if the other experimental variables are previously well established to allow for a more complete mechanistic understanding.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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