

Green Chemistry

Cutting-edge research for a greener sustainable future

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1. In this work, deep eutectic solvents (DESs) are introduced as non-volatile, cheap solvent-electrolyte systems with the potential to solubilize biomass for reductive electrosynthesis. The use of DES systems is a promising approach to reduce waste formation in organic electrosynthesis, often generated from supporting electrolyte salts and organic solvents.
2. The study showcases DESs as solvent-electrolyte system for electroreductive C-O cleavage of various lignin model ether compounds, achieving up to 97% phenol selectivity. The DES is reusable in at least three consecutive reactions without significant decrease in phenol selectivity.
3. Mass transfer in DES systems limit conversion and faradaic efficiency and future research should target improving the mass transfer for a wider use of DESs as electrolyte-systems. Furthermore, coupling reductive C-O cleavage with a productive counter reaction could increase the atom economy of the process allowing electroreductive biomass valorization as a next step.



Deep eutectic solvents as recyclable solvent-electrolyte systems for electroreductive C-O cleavage of lignin models

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Abstract

Deep eutectic solvents (DESs), formed from hydrogen bonding acceptors and donors, are investigated as recyclable solvent-electrolyte systems for the electroreductive cleavage of C-O bonds in lignin model ethers. The widely used DES composed of choline chloride and methyl urea demonstrates a suitable electrochemical window and high cathodic stability enabling efficient cleavage of benzyl phenyl ether, achieving up to 97% selectivity for phenol over three reaction cycles in a simple, undivided cell without catalysts or additives. Optimization studies show that the choice of electrode material significantly affects both conversion and yield. Furthermore, the method is applicable to a selection of lignin model ethers, with observed reactivity trends correlating to substrate structure and solubility. The work highlights the potential of low-cost DESs as novel, dual-function, and recyclable media for green electrosynthesis, providing a foundation for future advances in electrochemical lignin depolymerization. Notably, the approach reduces waste associated with traditional supporting electrolyte salts and solvents in electrosynthesis, and continued improvements in faradaic efficiency and process integration will unlock the full green potential of this novel strategy.

Keywords: Electrosynthesis, deep eutectic solvents, lignin model compounds, reduction C-O cleavage



Introduction

In electrochemical synthesis, electrons are used to activate molecules and drive redox reactions at ambient conditions, enabling the development of benign chemical production with minimized need for auxiliary reagents.^{1,2} This approach can offer greater energy efficiency, improved selectivity, and higher atom economy compared to traditional synthetic methods, making electrosynthesis promising as a more sustainable alternative to conventional approaches.^{3–6} However, electrosynthesis in organic solvents typically relies on supporting electrolytes such as, *e.g.*, perchlorates or quaternary ammonium salts, to ensure sufficient electric conductivity. While these supporting electrolytes are generally non-reactive and redox stable species, their interactions with electrode surfaces, reactant, and intermediates can influence reaction outcomes.⁷ Supporting electrolyte salts are often used in large excess and must be separated from the products after the reaction, leading to significant waste generation or downstream processing steps for their recovery that increases the complexity and costs of the synthetic process. The widespread use of organic solvents – often highly flammable and toxic – to dissolve large quantities of supporting electrolytes further limits the sustainability of organic electrosynthesis.^{8,9}

A range of strategies has been developed to mitigate the drawbacks associated with supporting electrolytes in electrosynthesis, including in situ generation of electrolytes,^{10,11} reduction of electrolyte concentration,¹² and the use of microflow cells with narrow inter-electrode gaps to maintain conductivity in the absence of electrolyte salts.^{13,14} Another promising approach involves the design of electrolyte systems that allow for easy separation and reuse (Figure 1A), such as solid bases (solid electrolytes)^{15–17} and immobilized electrolytes on polymer backbones (polyelectrolytes).¹⁸ While these methods facilitate straightforward separation via filtration, they still require a reaction solvent. In this context, alternative solvents capable of serving dual roles – as both solvent and electrolyte – are of particular interest, especially if they can be easily separated from the product and reused. Ionic liquids (ILs) exemplify such systems and have been applied in electrosynthesis for various transformations,¹⁹ including carboxylation^{20–22} and phosphorylation.²³ Nevertheless, the use of ILs in electrosynthesis is hampered by their low conductivity and high cost.¹⁹

Deep eutectic solvents (DESSs), formed by mixing a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) in a specific ratio to reach a eutectic point, share many properties with ILs but are significantly cheaper.^{24,25} The high thermal stability, low volatility and



immiscibility with organic solvents of DES, enable their recovery and recycling by various methods. These include practical methods such as liquid-liquid extraction, anti-solvent addition and short-path distillation,²⁶ rendering DESs promising as recyclable electrolyte/solvent systems. A distinct feature of DESs is their ability to solubilize biomass, making them highly attractive for biorefinery applications.^{27,28} In the context of lignin, DES can enable up to 50% (w/w) material dissolution, whereas in ILs similar results required higher temperatures.^{29–31} Lignin constitutes up to 30 wt% of lignocellulosic biomass, but remains underutilized in biorefinery applications, in contrast to the cellulose and hemicellulose fractions that have well-established industrial valorization pathways.³² Electrochemical oxidative depolymerization of lignin into low-molecular-weight chemicals has been widely studied in aqueous electrolytes with various electrocatalysts^{33–37}. In contrast, analogous reductive depolymerization of lignin is less explored, despite the potential advantages, such as production of value-added aromatics with high energy density due to increased hydrogen content.³⁸ Reports on reductive approaches for cleavage of dimeric lignin model compounds includes diphenyl ethers^{39–41} and β -O-4 models^{42–48} in aqueous electrolytes and organic electrolytes.

DESs have been studied as electrolytes in electrochemical applications, including battery chemistry^{49,50} and electrodeposition,⁵¹ their use in electrosynthesis remains limited (Figure 1B). Transformations in neat DES systems include the electrochemically assisted formation of bis(indoyl)methane,⁵² pyran,⁵³ and xanthene derivatives.⁵⁴ DES systems have also recently been successfully applied for electrochemical sulfonation,⁵⁵ allylation⁵⁶ and carboxylation.⁵⁷ Furthermore, oxidative electrochemical depolymerization of lignin have shown promise in DES-water mixtures^{58,59} and emulsions,⁶⁰ yielding vanillin and guaiacol as the major products. On the other hand, the C-O cleavage of a β -O-4 lignin model, 2-phenoxyacetophene, was studied by Cruz *et al.*⁶¹ under reductive conditions in a DES-H₂O electrolyte. While selective β -O-4 cleavage was not observed, it was shown that the electrocatalytic hydrogenation generated different product types depending on the cell type. Likewise, Zhang *et al.* studied electrocatalytic cleavage of the β -O-4 lignin model 2-phenoxy-1-phenylethanol, utilizing a nickel-cobalt catalyst in a DES-acetonitrile electrolyte, which enabled both C-O and C-C cleavage.⁶² Notably, DESs consisting of choline chloride and ethylene glycol have mostly been utilized, despite the large combinatorial space within composition of DESs. Thus, their full potential as integrated solvent-electrolyte systems (deep eutectic electrolytes) for direct electrochemical transformations remains largely unexplored.



In this work, we focus on the use of such deep eutectic electrolytes as medium for electroreductive C-O bond cleavage of an α -O-4 type lignin motif, utilizing benzyl phenyl ether as a model compound. Electrochemical reductive C-O cleavage of benzyl phenyl ether has previously been studied in a range of conventional solvents (Figure 1C). Using NaCl electrolyte in ethanol/water, Mahdavi *et al.* observed partial hydrogenation forming cyclohexane and toluene under reductive conditions.⁶³ Electrocatalytic hydrogenation of benzyl phenyl ether was also studied by Song *et al.* using a Rh/C catalyst in aqueous isopropanol, where hydrogenation of the aromatic ring was more prevalent than C-O cleavage.⁶⁴ Recently Karanwal *et al.* demonstrated efficient Pd-catalyzed hydrogenolysis using a perchloric acid electrolyte.⁶⁵ Selective reductive C-O cleavage of several lignin bond motifs was achieved by Wu and Huang, utilizing borohydride as a promotor in NMP/NaBF₄ electrolyte system.⁶⁶ In this case, mechanistic studies show that both borohydride and the solvent acts as proton sources for product formation. Lin *et al.* studied Ni-catalyzed C-O cleavage in methanol/NBu₄PF₆ electrolyte in both undivided and divided cells, showing that the phenol yield increased significantly by the use of a divided cell.⁶⁷ Furthermore, it was shown that Ni⁰ played a central role in facilitating C-O cleavage.⁶⁸ Besides, in an attempt to utilize more environmentally friendly electrolytes, Zhang *et al.* recently demonstrated C-O cleavage of benzyl phenyl ether in methanol, yielding up to 95% of benzaldehyde dimethyl acetal using NaBF₄ or NaCl as supporting electrolyte salts.^{69,70}

In this work, we investigate a selection of DESs as a benign combined solvent-electrolyte system for the electroreductive cleavage of C-O bonds in lignin model compounds (Figure 1D). A systematic study of benzyl phenyl ether **1a** with a α -O-4 type lignin motif reveals the effect that the DESs composition, reaction temperature, and electrode materials has on the yield and selectivity of phenol (**2a**) as target product. Among the tested systems, a DES composed of choline chloride-methyl urea enabled highly selective phenol formation – achieving 97% selectivity after passing 2.5 F of charge - without the need for catalysts or additives and using a simple undivided cell. Importantly, the DES could be reused for at least three consecutive cycles without observable degradation, highlighting its potential to serve as a low-cost, robust, and sustainable medium for lignin electro-valorization.



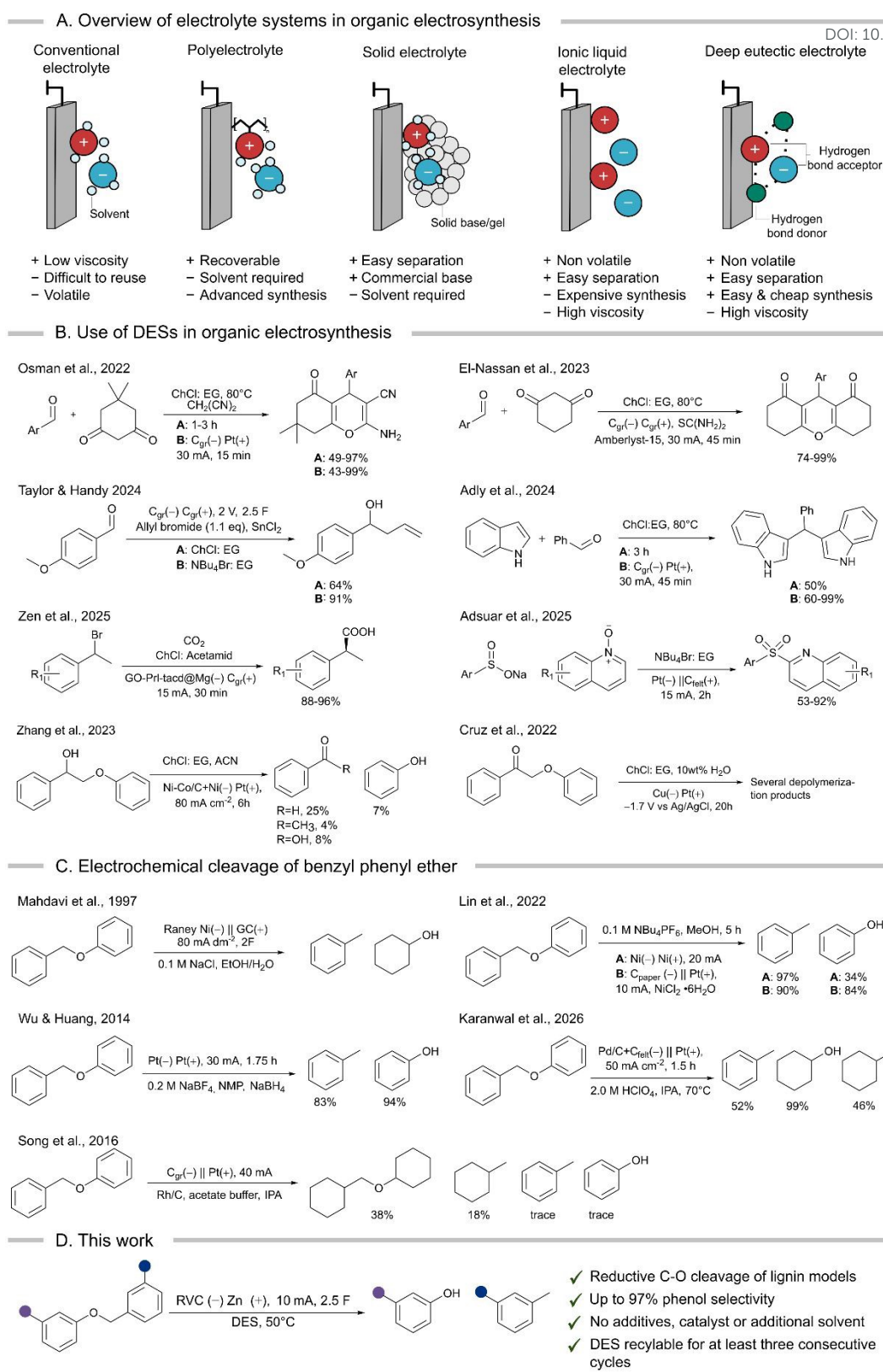


Figure 1: DESs as recyclable electrolytes for C-O cleavage. (a) Approaches to recyclable electrolytes in electrosynthesis. (b) Use of DESs in electrosynthesis with reported yields. (c) Electrochemical cleavage of benzyl phenyl ether (|| denotes a divided cell). (d) This work.



Results and discussion

Electrochemical properties of DES systems

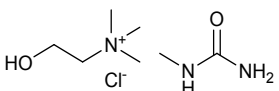
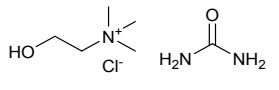
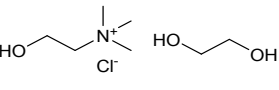
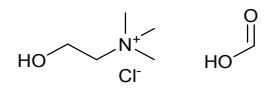
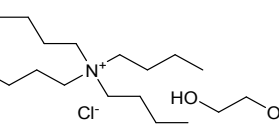
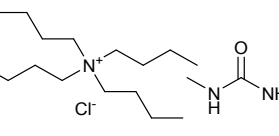
Six ammonium-based DESs (Table 1) were synthesized for their evaluation as electrolytes in reductive electrosynthesis (see SI for details). Choline chloride with *N*-methyl urea (DES-1) was selected due to its reported high cathodic stability,⁷¹ and its well-established analogues choline chloride with urea (DES-2) or ethylene glycol (DES-3) were assessed for comparison. DES-4, based on choline chloride and formic acid, was selected to expand the scope of hydrogen bond donors known to be beneficial in lignin applications.⁷² To investigate the role of the hydrogen bond acceptor, analogues with tetrabutylammonium counterions were chosen (DES-5 and DES-6) as this cation is commonly used in conventional electrolyte systems for organic electrosynthesis. All synthesized DES, except DES-6 was liquid at room temperature. Initially, the electrochemical redox potentials of the neat DESs were evaluated by cyclic voltammetry (CV) from which the anodic/cathodic limits and electrochemical stability window (ECW) was determined (see SI, Figures S4-9).

As may be expected, the nature of the HBD and HBA greatly influenced the electrochemical stability windows of the DESs (Table 1). For the choline chloride-based DESs (DES-1 to DES-4), the HBD significantly affected the cathodic limit that was found to increase in the order: formic acid (DES-4) < ethylene glycol (DES-3) < *N*-methyl urea (DES-1) ~ urea (DES-2) with a difference of 730 mV between DES-2 and DES-4. This trend is consistent with previous reports and clearly demonstrates that the cathodic stability is correlated to the nature of the HBD.⁷¹ The role of the HBA on the electrochemical window is less clear. When comparing DES-1 with DES-6 and DES-3 with DES-5 (Table 1, entries 1 vs 6 and 3 vs 5, respectively), the switch from choline chloride to tetrabutylammonium chloride as HBA resulted in a decrease of the anodic limit in the first case, while a slight increase is observed in the latter case. The same trend could be observed for the cathodic limit. The similar anodic limit of DES-3 to DES-6 could suggest that oxidation of chloride limits the anodic stability in these cases, whereas DES-1 and DES-2 display considerably higher anodic limits. As such, interactions between the HBD and HBA affect the electrochemical properties of a DES and likely play a role for their degradation, though this is not well understood.⁷¹ The combination of choline chloride and urea (DES-2) resulted in the largest ECW (4.49 V), while DES-5 showed the greatest cathodic stability, the latter being close to that of the conventional solvent/electrolyte system tetrabutylammonium hexafluorophosphate (NBu₄PF₆) in *N,N*-dimethylformamide (DMF) (Table 1, entries 5 vs 7).



In addition to electrochemical stability, the conductivity is another important factor for electrolyte systems as it affects cell resistance and faradaic efficiencies of the electrochemical transformation.⁷³ As seen in Table 1, DES-1, DES-2 and DES-5 display lower conductivities compared to the conventional electrolyte system (Table 1, entries 1, 2 and 5 vs 7), whereas the less viscous DES-3 and DES-4 display considerably higher values (Table 1, entries 3 and 4 vs 7) (see SI, Table S1 for viscosity data). It should be noted that the conductivity of the conventional electrolyte is dependent on the concentration of supporting electrolyte salts and comparisons with the neat DES systems in Table 1 should, thus, be done with caution.⁷⁴ In this case, the conductivity of the conventional electrolyte was carried out at a 0.1 M concentration of supporting electrolyte.

Table 1: Electrochemical properties of the synthesized DESs and a DMF/NBu₄PF₆ reference system.

Entry	System	HBA:HBD (1:2 molar ratio)	Cathodic limit (V vs. Fc ^{0/+}) ^a	Anodic limit (V vs. Fc ^{0/+}) ^a	ECW (V)	Conductivity (mS/cm) ^d
1	DES-1 ^b		-3.34	0.88	4.22	2.1
2	DES-2		-3.36	1.13	4.49	2.6
3	DES-3		-3.03	0.60	3.63	16
4	DES-4		-2.63	0.67	3.30	30
5	DES-5		-3.45	0.69	4.14	1.9
6	DES-6 ^c		-3.23	0.63	3.86	-
7	DMF/0.1M NBu ₄ PF ₆	-	-3.45	1.29	4.74	6.3

^a Limits determined for DESs by CV using a scan rate of 100 mV/s and a threshold current density of 0.5 mA/cm² at room temperature with a glassy carbon (GC) disk working electrode, saturated calomel reference electrode (SCE), and Pt wire counter electrode (details in SI, section 1.8). ^b CV measured at 30°C. ^c CV measured at 80°C. ^d Measured at 50°C (details in SI, section 1.9).



Evaluation of DES systems for C-O cleavage

As several of the examined DESs exhibited high cathodic stability and sufficient conductivity (Table 1), were all DESs that were liquid at room temperature (DES1-5) probed as electrolyte media for electroreductive C-O bond cleavage of the lignin model benzyl phenyl ether **1a** with an α -O-4 type lignin motif in an undivided cell under galvanostatic conditions (Figure 2). Molecular sieves were added to absorb residual water and thus minimize the competing cathodic hydrogen evolution reaction (HER). Compared to organic solvents, DESs are more viscous (see SI, Table S1) and a high surface area cathode material - reticular vitreous carbon (RVC) - was thus employed to facilitate mass transport (see SI for details). The most effective electrolysis was obtained with DES-1 as the electrolyte medium (39% conversion and 29% yield of **2a**). As a general trend, the conversion and phenol yield correlate with the cathodic stability of the DES, with the notable exception of DES-2. Interestingly, DES-5 shows similar results as DES-1 although it was assessed to be more cathodically stable than DES-1 (Table 1). To probe the origin of this behavior, the reduction of **1a** was studied in the different DES by means of CV (Figure 3). This assessment revealed that the onset reduction potential for **1a** in DES-1, DES-3 and DES-5 was positively shifted compared to the value in a DMF electrolyte (-3.19 V). In contrast, DES-2 and DES-4 afforded no shift in the reductive onset potential of **1a**. This finding is consistent with the lower conversions and yields observed for reductive electrolysis of **1a** in the latter two DESs, indicating that both electrochemical stability of the electrolyte and its interaction with the organic substrate is of importance for reaction outcome. The highest conversion of **1a** and the highest phenol yield (39 and 29%, respectively) was obtained in DES-1, in which the least negative onset potential of **1a** was observed. Such an anodic shift of the reduction potential is attractive as it enables the transformation to occur at milder conditions, suggesting that higher functional group tolerance and lower energy consumption may be possible.^{75,76} The promising synthetic results combined with the moderate hygroscopic nature of DES-1 (see SI, Table S1), this medium was chosen for the continued studies of reductive C-O bond cleavage in **1a**.



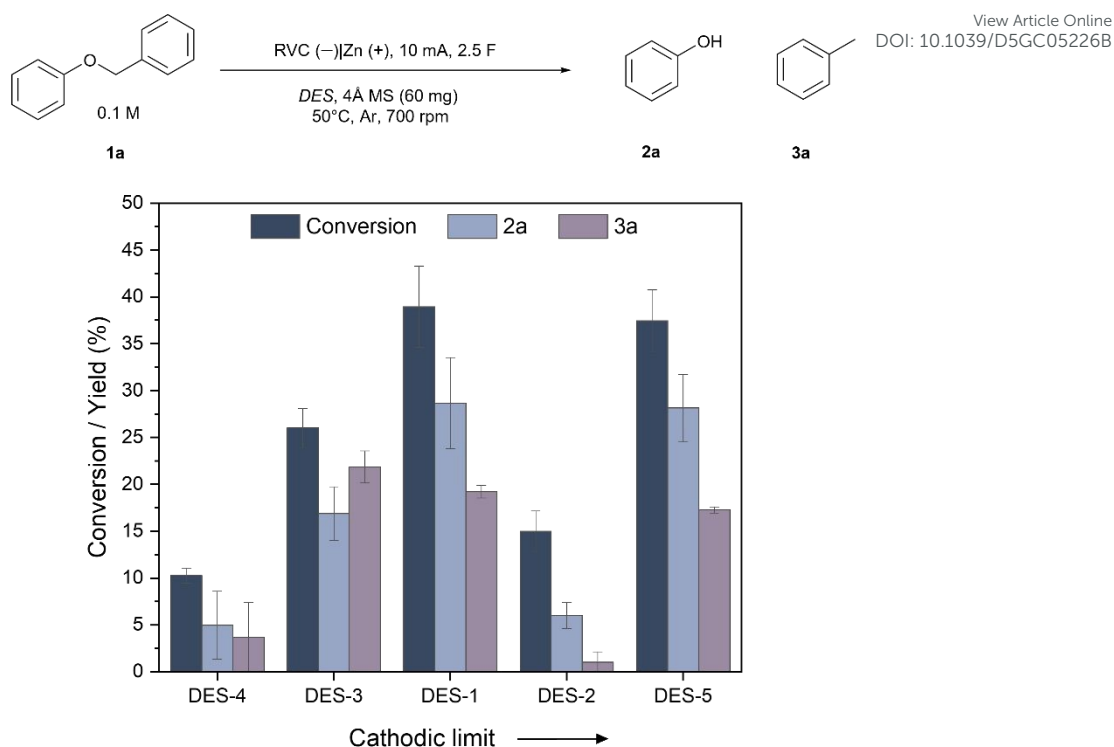


Figure 2: Screening of different DESs as solvent-electrolyte systems for C-O cleavage of benzyl phenyl ether **1a**. Conversion and yields are determined by HPLC analysis (SI, section 1.6 for details).

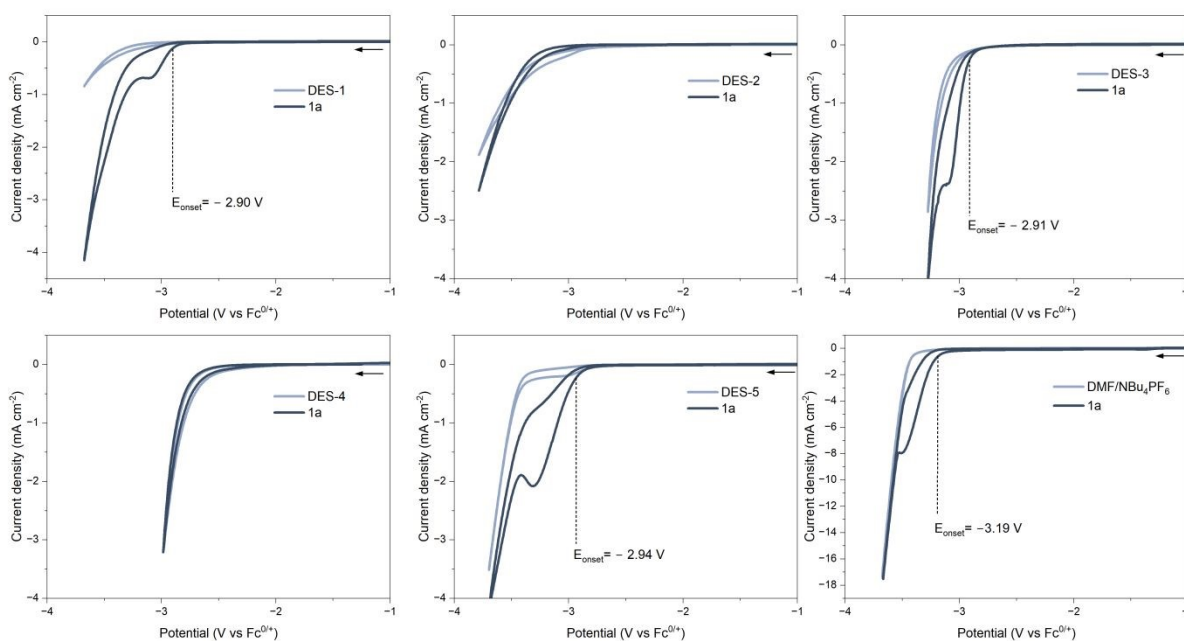


Figure 3: CVs of benzyl phenyl ether **1a** (80 mM) in DESs and conventional electrolyte (DMF, 0.1 M NBu_4PF_6 , 20 mM **1a**). Conditions: GC disk working electrode, SCE reference, and Pt wire counter electrode. The scan started at open circuit potential in a negative direction with a scan rate of 100 mV/s.



Optimization and reuse of DES-1 system for C-O cleavage

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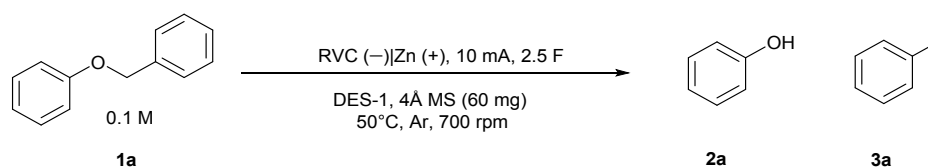
To further improve the conversion and product selectivity in the electroreduction of **1a** in DES-1, electrode materials and reaction conditions were screened (Table 2 and Figure 4). To ensure adequate reproducibility, each reaction was repeated at least twice (see SI, section 1.4 for details). Previous reports on electrochemical C-O bond cleavage of **1a** in conventional solvent/electrolyte systems had employed both carbon-,⁷⁷ Pt-,⁶⁶ and Ni-^{67,68} based cathodes (Figure 1C). With the DES-1 system, all carbon-based cathodes (Table 2, entries 1-3) resulted in product formation, whereas Ni (Table 2, entry 4) and stainless steel (SS) (Table 2, entry 5) cathodes failed to convert **1a**. However, compared to the other carbon-based electrodes, the product selectivity was lower using a graphite cathode (C_{gr}) (Table 2, entry 3 vs 1-2) and the conversion was found to decrease upon reuse (see SI, Table S3). This behavior occurred despite thorough electrode cleaning and polishing between reactions, possibly due to intercalation of ions in the graphite material. Likewise, a glassy carbon (GC) cathode (Table 2, entry 2) resulted in both lower substrate conversion and product selectivity compared to the use of a reticulated vitreous carbon (RVC) cathode, as the higher surface area of the latter likely results in improved diffusion and thus higher reaction rate.

To balance the net-cathodic transformation, the selection of the counter reaction is important to ensure efficient electrolysis.⁷⁸⁻⁸¹ Exchanging the sacrificial zinc anode with magnesium or aluminum electrodes (Table 2, entries 1 vs 6 and 7), resulted in lower product yields and selectivity. This result may correlate with the increased resistance observed, causing the cell potential to exceed the capacity of the external power supply and thereby preventing the passing of 2.5 F of charge during the experiments (for details see SI, Figure S2). The increased resistance may be understood in terms of anode passivation, as well as the lower solubility of Al³⁺ ions compared to Zn²⁺ ions in similar DESs.⁸² The lower oxidation potential of Zn compared to Al and Mg,⁸³ likely also contributes to higher product selectivity as oxidative side reactions may be more effectively suppressed. For reductive C-O bond activation, borohydride species have previously been demonstrated to act as anodic fuel,⁸¹ as well as hydrogen donors.⁶⁶ However, the addition of borohydride to the DES electrolyte together with the use of a Zn anode resulted in lower product selectivity (Table 2, entry 8). Similarly, reduced phenol selectivity was observed when an inert carbon-based anode was used together with borohydride (see SI, Table S3). In contrast, product selectivity was unaffected by the omission of molecular sieves (Table 2, entry 9), whereas the conversion of **1a** decreased, likely due to residual water leading to undesired hydrogen evolution. As expected, the reaction did not proceed in the



absence of current (Table 2, entry 10). Notably, the results in Table 2 show that the yield of toluene was consistently lower compared to that of phenol. To probe if this observation was the result of a lack of H-donors in the system, additives such as NaHCO₃ and NBu₄PF₆ (see SI, Table S3 for details) were assessed but did not improve the toluene yield. No benzylic coupling products, nor chlorinated or oxidized products could be detected in the reaction mixture by HPLC (SI, Figure S23) or GC-MS (SI, Figure S41). Similarly, reduction products, such as cyclohexanol or 1-methylcyclohexane, could not be detected under these conditions by GC-MS. However, in addition to **1a**, **2a** and **3a**, GC-MS analysis showed trace amounts of the 1-methylcyclohexa-1,4-diene, a Birch reduction product of toluene, which has previously been reported as a side-product for aryl ether cleavage.⁶⁶ These results suggest that the observed lower yield of toluene compared to phenol stems from a combination of continued reduction and higher volatility of the former, which may lead to an underestimation of the true yield.

Table 2: Optimization of C-O cleavage of benzyl phenyl ether **1a** in DES-1.



Entry	Deviation	Yield (Selectivity) (%) ^a		Conversion (%) ^a
		2a	3a	
1	None	29 (73)	19 (50)	39
2	GC cathode	14 (50)	5 (17)	27
3	C _{gr} cathode	6 (17)	6 (16)	35
4	Ni cathode	-	-	<5
5	SS cathode	-	-	<5
6	Mg anode ^b	3 (14)	2 (14)	19
7	Al anode ^b	10 (43)	10 (41)	24
8	NBu ₄ BH ₄ (0.3 eq.)	28 (63)	14 (31)	44
9	No MS	25 (74)	16 (45)	34
10	No current	-	-	<5

^a Conversions and product yields are determined by HPLC analysis (see SI, section 1.6) and are average of at least two identical experiments (see SI, Table S3). ^b Resistance too high to pass 2.5 F (see details in SI, Table S3 and Figure S2). GC: glassy carbon, C_{gr}: graphite, MS: molecular sieves, RVC: reticular vitreous carbon, SS: stainless steel.



Further optimization of the reaction parameters for the electroreduction of **1a** through a design of experiment (DoE) approach with temperature, current, and charge as factors, indicated that temperature was a significant parameter for conversion and product yield (SI, Table S4 and Figure S3). Although the conductivity of DESs generally increases with temperature, higher reaction temperatures resulted in lower conversion and yield. Performing the reaction at lower temperatures of 30-40°C proved unviable due to solidification of DES-1 that has a freezing point of 29°C.⁸⁴ Additional experiments revealed that increasing the charge passed through the cell to 5 F increased product selectivity, whereas higher charges resulted in decreased selectivity, likely due to the onset of side-reactions (Figure 4a). In contrast, the conversion of **1a** remained largely unaffected by increased charge, suggesting that mass transfer at the electrode surface may limit the overall conversion rate. This hypothesis was supported by observations, indicating that an increase in stirring rate up to 1200 rpm resulted in higher conversion and product yields (Figure 4b). A further increase in stirring rate to 1500 rpm had marginal effect on conversion but appeared to positively influence the selectivity in product formation, resulting in phenol selectivity of 97%. This increase in selectivity as a function of stirring rate may be attributed to a decreased thickness of the diffusion layer, resulting in improved transport of formed products away from the electrode.⁸⁵ Based on high selectivity for **2a** achieved at 50°C with 1500 rpm stirring rate passing 2.5 F, these conditions were selected as optimal for subsequent experiments.

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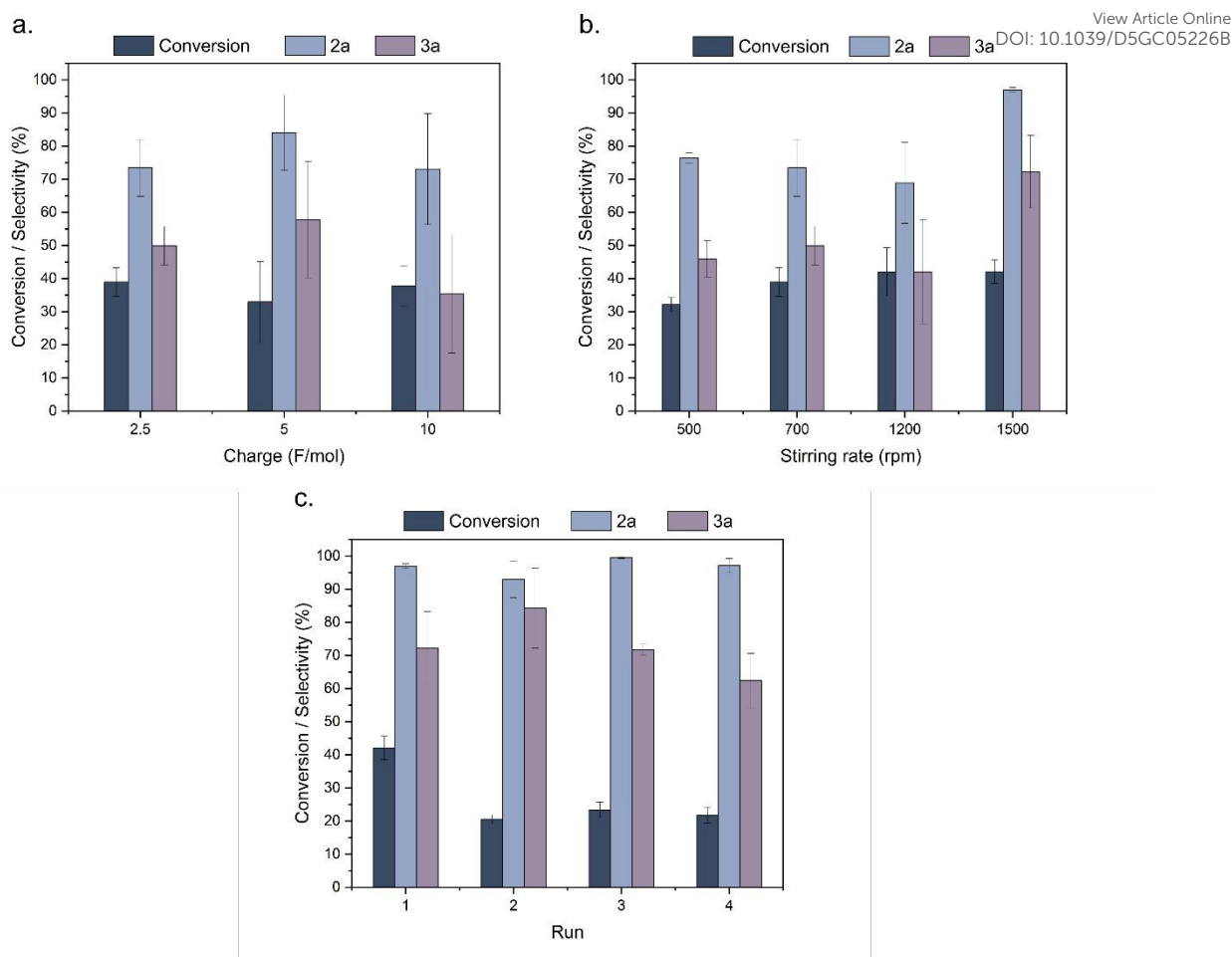


Figure 4: Optimization and reuse of DES-1 system for C-O cleavage of benzyl phenyl ether **1a**. a. Effect of charge (2.5-10 F, 10 mA, 700 rpm). b. Effect of stirring rate (500-1500 rpm, 10 mA, 2.5 F). c. Recycling of DES-1 (2.5 F, 10 mA, 1500 rpm).

To evaluate the recyclability of DES-1, the solvent was collected after electrochemical reaction and separated from the products by extraction before reuse in subsequent reactions (see SI, section 1.5 for details). These recycling experiments demonstrated that DES-1 could be reused in at least three consecutive reactions without significant change in phenol selectivity (Figure 4c). However, a gradual decrease in the conversion of **1a** was observed upon recycling, likely due to the accumulation of residual water in the recycled DES – a factor that could not be fully mitigated by the addition of molecular sieves (see SI, Table S2). Analysis of the recycled DES-1 by ^1H nuclear magnetic resonance (NMR) spectroscopy (see SI, Figure S34) showed no evidence of structural decomposition during electrolysis. Instead, ^1H -NMR of recycled DES showed changes in the chemical shifts that can be attributed to increased water content (SI, Figure S34 and S35).^{86,87} While additional work is required for effective drying, these results suggest that DES-1 can be used as a recyclable electrolyte. With further optimization of the DES recovery method via the wide range of available routes, including distillation, extraction



and anti-solvent addition, there is great potential for more sustainable and user-friendly reuse of this electrolyte system compared to what is possible for organic solvents with supporting electrolyte salts.

The use of a conventional electrolyte (DMF/NBu₄PF₆) instead of DES-1 under optimized conditions (1500 rpm, 2.5 F, RVC(-)|Zn(+)), resulted in higher conversion of **1a** (71% vs 42%), likely due to the lower viscosity of the former that leads to improved mass transport. Nevertheless, lower selectivities for phenol (69% vs 97%) and toluene (57% vs 72%) were observed in the conventional electrolyte compared to DES-1 (see SI, Table S3 for details). This finding may potentially be attributed to DES stabilization of formed products via hydrogen bonding,⁸⁸ thereby preventing electrochemical degradation. Similarly, the use of DES-1 resulted in lower conversion rates compared to earlier reported protocols on reductive C-O cleavage of **1a** in conventional electrolyte (Figure 1C), which all achieved near full conversion.^{63–70} However, in terms of phenol selectivity the current protocol achieves similar - or even higher - selectivity compared to these protocols without the use of catalysts, additives or divided cell configurations.

C-O cleavage of other lignin model ethers in DES-1 system

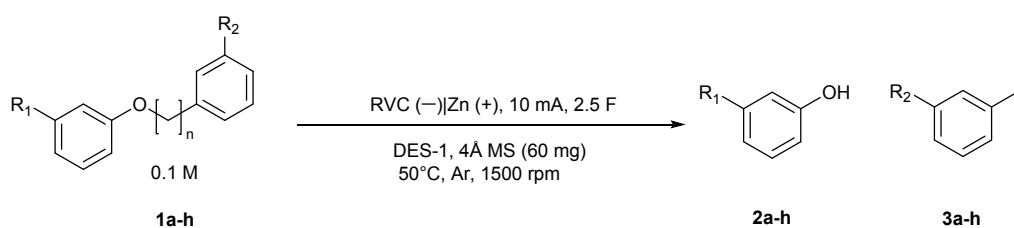
With optimized conditions for the DES-1 system at hand, the reductive C-O bond cleavage for a selection of other lignin model ether compounds was examined (Table 3). For the methoxy derivative **1b** (Table 3, entry 2), a phenol selectivity identical to that of **1a** (Table 3, entry 1) was observed, while a considerably lower selectivity was observed for the isomer **1c** (Table 3, entry 3). Due to the similar reductive onset potential for **1b** and **1c** (SI, Figures S13 and S14), steric effects are likely the cause of these selectivity differences. The ester-substituted **1d** resulted in similar phenol selectivity as **1c** (Table 3, entry 4), whereas the isomeric **1e** (Table 3, entry 5) displayed a low solubility in DES-1 and remained unconverted during electrolysis. With a hydroxy group in *meta* position, **1f** resulted in lower selectivity for the phenolic product while the toluene selectivity was moderate (Table 3, entry 6). With the hydroxy group instead placed in *para* position, **1g** resulted in high selectivity for toluene and moderate selectivity for the phenolic product (Table 3, entry 7). With the addition of a methoxy group in *meta* position, **1h** resulted in similar conversion with overall lower product yields (Table 3, entry 8). The lower selectivity of the phenolic product in these cases compared to that of the benchmark substrate **1a** could be the result of faster product degradation of diphenols compared to phenol.⁸⁹ The C-O bond cleavage of the β-O-4 type model **1i** (Table 3, entry 9) displayed good

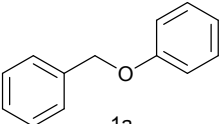

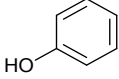
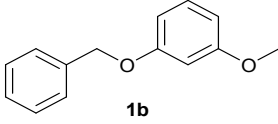

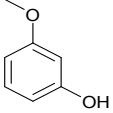
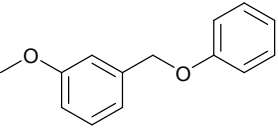
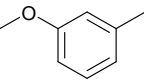
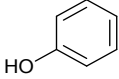
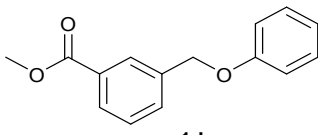
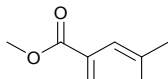
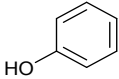
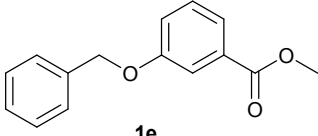
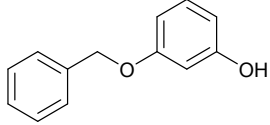

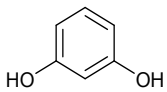
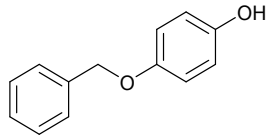

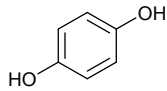
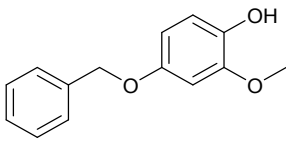

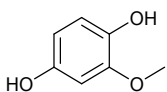


phenol selectivity (67%), albeit low conversion, under the applied conditions. Conversely, compound **1j** (Table 3, entry 10) did not convert under the applied conditions, likely due to its highly negative reduction potential that lies outside the solvent stability window of DES-1 (see SI, Figure S21). For the same reason, the C-O bond cleavage of the diphenyl ether **1k** with a 4-O-5 type lignin motif was sluggish and unselective (Table 3, entry 11; see SI, Figure S22). Overall, reductive C-O bond cleavage of a range of lignin model compounds showed promising results for α -O-4 cleavage, considering that the conditions were not optimized individually for every compound.

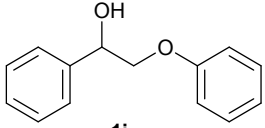
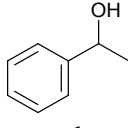
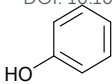
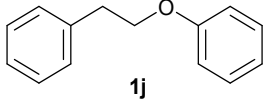
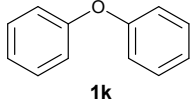

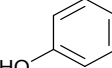
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Table 3: Electrochemical reductive C-O cleavage of lignin model ethers in DES-1.View Article Online
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Entry	Substrate	Conversion (%)	Yield (selectivity) (%) ^a	
1	 1a	42	 30 (72)	 41 (97)
2	 1b	25	 14 (53)	 25 (97)
3	 1c	31	 4 (13)	 13 (43)
4	 1d	57	 n.d.	 31 (55)
5	 1e	-	-	-
6	 1f	43	 16 (37)	 7 (16)
7	 1g	25	 23 (92)	 11 (44)
8	 1h	27	 21 (78)	 3 (12)



9	 1i	16	 n.d.	View Article Online DOI: 10.1039/D5GC05226B  11 (67)
10	 1j	-	-	-
11	 1k	24	 n.d.	 2 (10)

^a Conversions and yields are determined by HPLC analysis (see SI, section 1.6). n.d.: Not detected.

Conclusions

A series of DESs, composed of ammonium salts as hydrogen bond acceptors (HBAs) and diols or ureas as hydrogen bond donors (HBDs), were investigated as novel solvent-electrolyte systems for electroreductive C-O bond cleavage of lignin model ether compounds. Relying on its high cathodic stability, choline chloride-methyl urea (DES-1) was pertinent for electrochemical cleavage of phenyl ethers, enabling selectivities up to 97% towards phenol after optimization of various reaction parameters. Notably, this product selectivity was achieved without the use of additives or catalysts in a simple undivided cell setup and DES-1 could successfully be reused with maintained product selectivity over three consecutive reaction cycles. Furthermore, the DES-1 electrolyte was successfully used for electroreductive C-O bond cleavage in a selection of lignin model compounds. While improvements of mass transfer, faradaic efficiencies and reduced water content in recycled DES are challenges to address in future work, this study serves as a starting point for exploration of electroreductive transformations in DES media, including lignin depolymerization.

Author contributions

AKS: Investigation, methodology, validation, visualization, writing – original draft. **HL:** Conceptualization, funding acquisition, supervision, writing – review & editing. **AR:** Project administration, conceptualization, funding acquisition, supervision, writing – review & editing.



Conflicts of interest

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There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

Acknowledgements

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Data availability statement

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The data supporting this article have been included as part of the Supplementary Information.

