





# Effect of alkali-metal cation on oxygen adsorption at Pt single-crystal electrodes in non-aqueous electrolytes

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The effect of Group 1 alkali-metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$ ) on the oxygen reduction and evolution reactions (ORR and OER) using dimethyl sulfoxide (DMSO)-based electrolytes was investigated. Cyclic voltammetry (CV) utilising different Pt-electrode surfaces (polycrystalline Pt, Pt(111) and Pt(100)) was undertaken to investigate the influence of surface structure upon the ORR and OER. For  $\text{K}^+$  and  $\text{Cs}^+$ , negligible variation in the CV response (in contrast to  $\text{Na}^+$ ) was observed using Pt(111), Pt(100) and Pt(poly) electrodes, consistent with a weak surface-metal/superoxide complex interaction. Indeed, changes in the half-wave potentials ( $E_{1/2}$ ) and relative intensities of the redox peaks corresponding to superoxy ( $\text{O}_2^-$ ) and peroxy ( $\text{O}_2^{2-}$ ) ion formation were consistent with a solution-mediated mechanism for larger cations, such as  $\text{Cs}^+$ . Support for this finding was obtained *via in situ* shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS). During the ORR and in the presence of  $\text{Cs}^+$ ,  $\text{O}_2^-$  and weakly adsorbed caesium superoxide ( $\text{CsO}_2$ ) species were detected. Because DMSO was found to strongly interact with the surface at potentials associated with the ORR,  $\text{CsO}_2$  was readily displaced at more negative potentials *via* increased solvent adsorption at the surface. This finding highlights the important impact of the solvent during ORR/OER reactions.

## Introduction

Lithium–oxygen ( $\text{Li-O}_2$ ) batteries have become of particular interest due to their high theoretical specific energy ( $3505 \text{ W h kg}^{-1}$  for the non-aqueous system) compared to the commonly used Li-ion batteries.<sup>1</sup> Studies of  $\text{Li-O}_2$  systems in

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non-aqueous electrolytes have shown that on Au, Pt, and C surfaces, lithium peroxide ( $\text{Li}_2\text{O}_2$ ) is the main product of the oxygen reduction reaction (ORR).<sup>2-5</sup> The precipitation of solid  $\text{Li}_2\text{O}_2$  during the ORR passivates the electrode surface and blocks the electrode active sites, reducing any catalytic effect of the surface, which leads to the occurrence of parasitic reactions associated with the generation of singlet oxygen.<sup>2,6-8</sup>

In 2013, Hartmann *et al.*<sup>9</sup> and Ren *et al.*<sup>10</sup> demonstrated that the irreversibility presented by the two-electron reduction of  $\text{O}_2$  to  $\text{Li}_2\text{O}_2$  could be improved by the formation of an oxygen/superoxide redox couple that enables a single-electron reversible oxygen reduction reaction/oxygen evolution reaction (ORR/OER) process with high specific energy ( $w_{\text{th}} = 1605 \text{ W h kg}^{-1}$  for  $\text{Na}_2\text{O}_2$ )<sup>9</sup> and avoids the formation of solid peroxide species that passivate the electrode surface.

In non-aqueous  $\text{Li}^+$ -containing electrolytes, control of the product stability and reduced oxygen species<sup>11,12</sup> through electrolyte solvation can be achieved by using solvents with increased Gutmann donor numbers.<sup>13,14</sup> High Gutmann-donor-number solvents allow the formation of  $\text{Li}^+/\text{O}_2^-$  ion pairs that react within the double layer, offering a preferred solution-based mechanism that avoids the passivation of the electrode and enhances the sluggish kinetics of the ORR.<sup>15</sup> The reversible formation of superoxide ( $\text{O}_2^-$ ) and peroxide ( $\text{O}_2^{2-}$ ) species has been detected on charge/discharge as the main products, together with some minor degradation observed over time for Li systems in dimethyl sulfoxide (DMSO).<sup>16,17</sup> DMSO presents a relatively high Gutmann donor number of  $29.8 \text{ kcal mol}^{-1}$ ,<sup>18,19</sup> based on the nucleophilic properties of the solvent and high stability.<sup>20</sup>

The size of the cations has been demonstrated to affect the ORR activity.<sup>27-32</sup> In aqueous systems, the cation hydration energy and non-covalent interactions between hydrated alkali-metal cations and  $\text{OH}_{\text{ads}}$  have been highlighted in this regard.<sup>21-23</sup> In Li-containing aprotic electrolytes, the ORR occurs almost exclusively with  $\text{Li}_2\text{O}_2$  as the reaction product.<sup>3,4</sup> Conversely, as one moves down the Group 1 metals, the reaction mechanism favours the formation of significant amounts of both  $\text{O}_2^{2-}$  and  $\text{O}_2^-$  species.<sup>24,25</sup> Indeed, within aprotic electrolytes, the ORR pathway has also been proved to depend on the cation size.<sup>9,10,26</sup> Studies of the Group 1 alkali metals have mostly focused on the smaller cations with investigations being predominantly confined to  $\text{Li}^+$  and  $\text{Na}^+$ .<sup>24,27-31</sup>  $\text{K}-\text{O}_2$  batteries<sup>32-34</sup> have attracted recent interest due to the reduced overpotential reported in the absence of catalysts and redox mediators compared to  $\text{Li}-\text{O}_2$  batteries.<sup>10</sup> Nevertheless, despite the ongoing investigations into the ORR, observation of mechanistic details at the interface for different cations remains elusive.<sup>35-37</sup>

Pt has been demonstrated to be one of the most efficient catalysts for the ORR in both aqueous and aprotic electrolytes on model systems.<sup>38-40</sup> In the past decade, *in situ* shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) has proven to be a powerful method to detect surface intermediates.<sup>41,42</sup> Specifically, *in situ* SHINERS studies on Pt single-crystal electrodes have been successfully used to investigate the adsorption of ORR intermediates in aqueous electrolytes<sup>43-45</sup> and also the  $\text{Na}-\text{O}_2$  non-aqueous system.<sup>4,24</sup> However, despite the success of this approach, there is still a paucity of combined single-crystal/*in situ* SHINERS investigations involving non-aqueous electrolytes to afford a fundamental molecular level insight into the ORR processes associated with metal-oxygen battery systems, probably due to the experimental challenges



that such studies present. Hence, in this work, we perform a qualitative study on the effect that the cation size has on the ORR and OER using such an approach. From SHINERS measurements, the key role that DMSO solvent molecules play in the displacement of adsorbed Cs-cation-superoxide moieties, formed in the initial oxygen reduction step, is demonstrated. Together with cyclic voltammetry (CV) data, showing negligible surface structural sensitivity towards reduction processes involving caesium and oxygen, a strong contrast with the analogous sodium-cation/oxygen redox system is revealed.

## Experimental

### Chemicals

Dimethyl sulfoxide (DMSO) (>99.9% Hi-Dry®, ROMIL), dried and purified by distillation, was stored inside a glovebox over molecular sieves to ensure an H<sub>2</sub>O content <4 ppm. Alkali-metal salts NaClO<sub>4</sub> (≥98.0%), KClO<sub>4</sub> (≥99.99%), and CsClO<sub>4</sub> (≥99.995%), from Sigma-Aldrich, were dried under vacuum at 80 °C overnight and stored inside a glovebox prior to use. Up to N5-purity Ar (≥99.998%, BOC) and O<sub>2</sub> (≥99.999%, BOC) gases, dried by passing through a desiccant (P<sub>2</sub>O<sub>5</sub>)-filled drying tube, were used for purging and bubbling the electrolytes, respectively, whilst not contaminating the glovebox atmosphere.

### Pt single-crystal preparation

Clavilier<sup>46</sup> half-bead Pt(111) and (100) single crystals were annealed with a butane flame and then cooled in a bubbler containing Milli-Q® water and a steady flow of 5% H<sub>2</sub> in Ar to produce a well-ordered surface, and subsequently quenched with a drop of Milli-Q® water (18.2 MΩ cm resistivity). The single crystal was then dipped in 1 mM NaBr (≥99.0%, Sigma-Aldrich) solution, to protect the surface *via* the formation of an irreversibly adsorbed bromine adlayer (Fig. 1).<sup>47</sup> The electrode was then dried under vacuum, transferred to a glovebox, and cycled 5–10 times to achieve a clean electrode surface, free of Br adatoms on the surface.

### Polycrystalline Pt preparation

Pt polycrystalline disk electrodes embedded in polyether ether ketone (PEEK) were polished using three different suspensions of decreasing-grain-size alumina (0.1 μm, 0.3 μm and 0.05 μm), then rinsed with ethanol and Milli-Q® water, and finally sonicated in water. The Pt(poly) electrodes were dried at 80 °C overnight under vacuum and then introduced into a glovebox (argon atmosphere; O<sub>2</sub>, H<sub>2</sub>O <0.1 ppm).

### Meniscus configuration

Pt half-bead single crystals were used under a meniscus configuration to ensure that the voltammetric profile corresponded exclusively to the well-oriented face of the electrode. The meniscus configuration avoids voltammetric features originating from the poly-oriented sides of the electrode, as depicted in Fig. 2a. To address the role of the meniscus<sup>48</sup> in O<sub>2</sub> diffusion during the ORR/OER, Pt(poly) electrodes have also been used in the traditional configuration, inserted flat in the electrolyte, as represented in Fig. 2b.



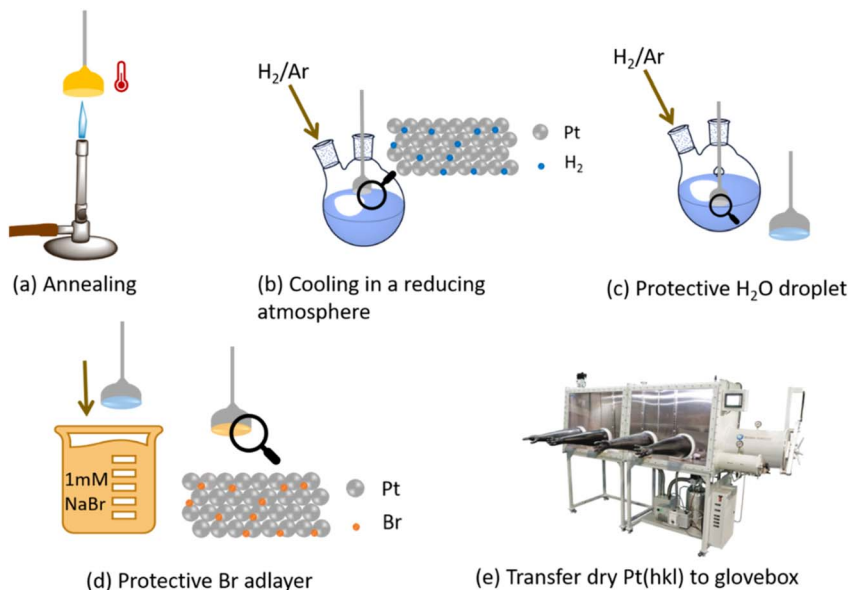


Fig. 1 Schematic description of single-crystal preparation for non-aqueous electrochemical studies. Reproduced from Galloway *et al.*<sup>24</sup> with permission from the Royal Society of Chemistry.

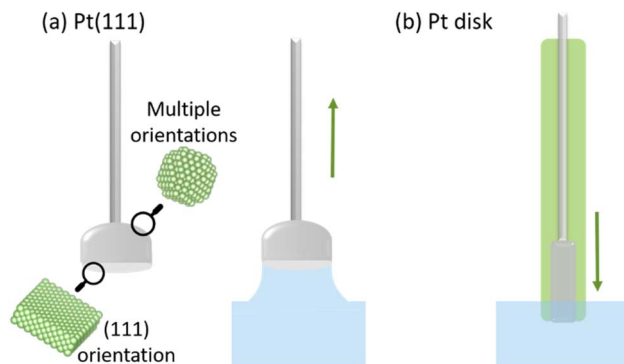


Fig. 2 (a) Schematic of a Pt single-crystal electrode with a (111) facet on the flat side under meniscus configuration. Hard-sphere model made with VESTA software.<sup>49</sup> (b) Schematic of a Pt polycrystalline disk electrode in contact with the electrolyte.

## Electrochemistry

Electrochemical experiments were conducted using a BioLogic (VSP-100) potentiostat in an Ar glovebox with moisture levels <1 ppm. Cyclic voltammetry experiments in the present study were carried out in a standard 3-electrode electrochemical cell. A silver wire was used as a pseudo-reference electrode. The Ag/Ag<sup>+</sup> couple was calibrated with the ferrocene/ferrocenium redox couple ( $E_{\text{Fc}/\text{Fc}^+}^0 = +680$  mV vs. SHE in DMSO).<sup>50</sup> All potentials are displayed vs. the calibrated Ag/Ag<sup>+</sup> redox couple to allow accurate comparison between experiments.



## Synthesis of shell-isolated nanoparticles for enhanced Raman spectroscopy

The synthesis of the Au core was carried out using the Turkevich–Frens citrate-reduction method.<sup>51–53</sup> 200 mL of a solution containing 0.01%  $\text{HAuCl}_4 \cdot n\text{H}_2\text{O}$  (99.995%, Sigma-Aldrich) were heated under vigorous stirring until boiling. 1.5 mL of a freshly prepared 1%  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  ( $\geq 99.5\%$ , Sigma-Aldrich) solution were immediately added to achieve a nanoparticle size of approximately  $\sim 55$  nm. The protocol developed by Liz-Marzán and co-workers<sup>54,55</sup> and used by Li *et al.*<sup>56</sup> for SHINERS was followed for  $\text{SiO}_2$  shell synthesis. Suitability of the silica shells for SHINERS was checked *via* the detection or absence of a Raman-active molecule (pyridine) on Au and Si substrates, respectively.<sup>42</sup>

### *In situ* Raman measurements

Raman measurements were carried out with a Raman spectrometer (Renishaw inVia) with an inverted microscope *via* a  $50\times$  objective (Leica), using a 633 nm laser with an exposure time of 10 s and 5 acquisitions. Pt wire was used in the spectro-electrochemical cell as a counter electrode and Ag wire as a reference. Long sealing screw caps were used to both isolate the cell and avoid any contaminants from dissolving into the electrolyte.

## Results and discussion

Pt(111) cyclic voltammetry in 0.1 M  $\text{NaClO}_4$  in DMSO electrolyte is displayed in Fig. 3. All the voltammetric features observed correspond exclusively to the adsorption of oxygen species onto the Pt electrode surface, as can be gleaned by the lack of faradaic current in the Ar-purged electrolyte.

The  $\text{Na-O}_2$  system on Pt basal planes has been previously studied in detail and the reaction mechanisms have been identified through *in situ* Raman microscopy.<sup>24</sup> The electrochemical behaviour of different single-crystal facets demonstrated that both  $\text{O}_2^-$  and  $\text{O}_2^{2-}$  species are formed during the ORR in the presence of  $\text{Na}^+$ . In agreement with the literature,<sup>11</sup> for Pt(111) the peak at  $-0.55$  V (I) observed in the reduction sweep in Fig. 3 corresponds to the reduction of  $\text{O}_2$  *via* formation of metal- $\text{O}_2^-$ , according to:

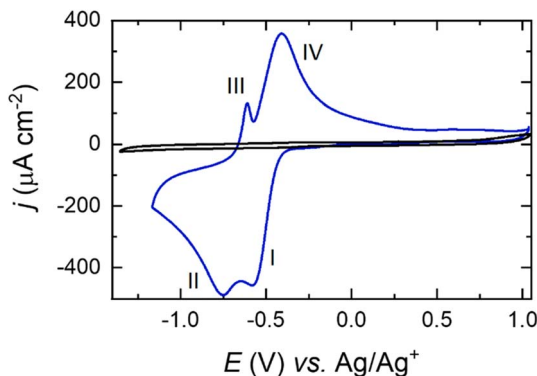
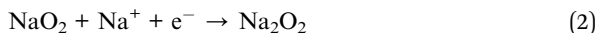


Fig. 3 Cyclic voltammograms of a Pt(111) electrode in a solution containing 0.1 M  $\text{NaClO}_4$  in DMSO, for Ar- (black) and  $\text{O}_2$ - (blue) saturated solutions. Scan rate:  $50 \text{ mV s}^{-1}$  at  $23^\circ\text{C}$ .

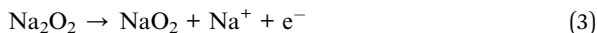




The second reduction peak at around  $-0.75$  V (II) corresponds to a second electron reduction that forms the metal- $\text{O}_2^{2-}$ :<sup>57</sup>



In the oxidation sweep, two peaks at  $-0.60$  V (III) and  $-0.40$  V (IV) are observed, which constitute the OER:



As with  $\text{Na}^+$ , for  $\text{K}^+$  and  $\text{Cs}^+$ , the ORR proceeds *via* two quasi-reversible electrochemical processes with two main reduction steps involving the formation of  $\text{O}_2^-$  and  $\text{O}_2^{2-}$  species (Fig. 4).<sup>57-61</sup>

The half-wave potential ( $E_{1/2}$ ) corresponding to the ion-pair formation between the alkali metal and  $\text{O}_2^-$  shifts towards more negative potentials for smaller cations ( $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$  - Table 1), while the  $E_{1/2}$  corresponding to the formation of  $\text{O}_2^{2-}$  follows the opposite trend (Table 2).

With a  $\text{Na}^+$ -containing electrolyte, Galloway *et al.*<sup>24</sup> studied the adsorption of species using different Pt(*hkl*) surfaces and demonstrated the surface specificity

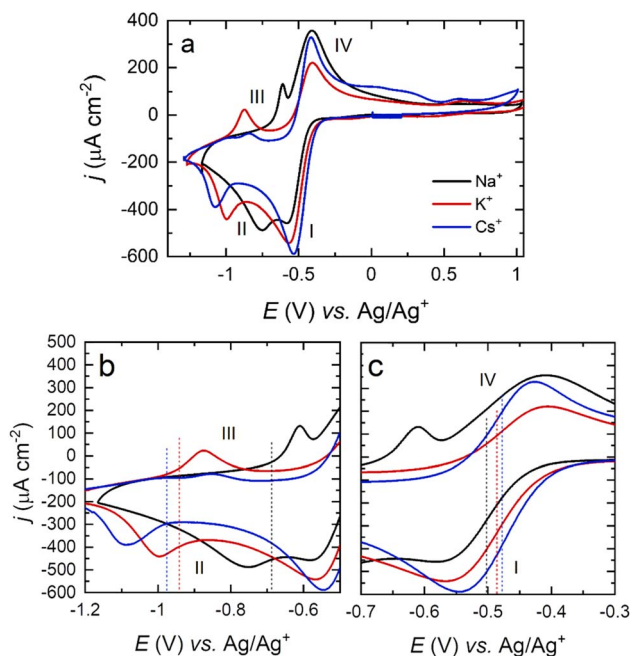


Fig. 4 (a) Cyclic voltammograms of a Pt(111) electrode in an  $\text{O}_2$ -saturated DMSO solution containing 0.1 M  $\text{NaClO}_4$  (black),  $\text{KClO}_4$  (red) and  $\text{CsClO}_4$  (blue). Scan rate:  $50 \text{ mV s}^{-1}$ . Expanded view of the peaks relating to the formation of  $\text{O}_2^{2-}$  (b) and  $\text{O}_2^-$  (c). Dotted lines represent the calculated  $E_{1/2}$  of the ORR half reactions for  $\text{Na}^+$  (black),  $\text{K}^+$  (red) and  $\text{Cs}^+$  (blue).



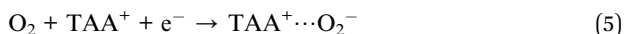
**Table 1** Ionic radii of alkali metals Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>. Values taken from the literature<sup>62</sup> are given in Ångström

Group 1 metal ion	Ionic radii (Å)
Na <sup>+</sup>	1.02
K <sup>+</sup>	1.38
Cs <sup>+</sup>	1.67

**Table 2** Half-wave peak potential for the formation of superoxide and peroxide species among different alkali cation sizes, for Pt(111) and Pt(poly). Values have been taken from the peak potentials ( $E_{1/2} = \frac{E_{\text{anodic}} + E_{\text{cathodic}}}{2}$ ) presented in Fig. 4 for Pt(111) and Fig. 5 for Pt(poly)

	NaO <sub>2</sub>	KO <sub>2</sub>	CsO <sub>2</sub>	Na <sub>2</sub> O <sub>2</sub>	K <sub>2</sub> O <sub>2</sub>	Cs <sub>2</sub> O <sub>2</sub>
Pt(111)	−0.50 V	−0.48 V	−0.47 V	−0.69 V	−0.93 V	−0.97 V
Pt(poly)	−0.53 V	−0.52 V	−0.50 V	−0.71 V	−0.90 V	−0.93 V

of Na<sup>+</sup>-ORR on Pt electrodes. In contrast, in the presence of cations larger than Cs<sup>+</sup>, such as tetraalkylammonium (TAA<sup>+</sup>) (ionic radius of 3.22 Å for tetramethylammonium (TMA<sup>+</sup>)),<sup>63,64</sup> the ORR is a highly reversible (less negative  $E_{1/2}$ ) one-electron process that involves the O<sub>2</sub>/O<sub>2</sub><sup>−</sup> couple,<sup>65–67</sup> according to:



Under steady-state conditions, Welford *et al.*<sup>68</sup> reported that the formation of O<sub>2</sub><sup>−</sup> is limited by the diffusion of O<sub>2</sub> through the three-phase boundary O<sub>2</sub>|electrode|electrolyte through the hanging meniscus in TAA<sup>+</sup>-containing electrolytes with Au(111). These results suggest that the O<sub>2</sub><sup>−</sup> species formation occurs exclusively *via* a solution-preferred mechanism limited by the diffusion of O<sub>2</sub>, *i.e.*, with low surface specificity compared to Na<sup>+</sup>.

In this paper, we suggest that the differences in the voltammetric response among alkali cations (Fig. 4) are due to a surface-mediated ORR for smaller cations, while larger cations prefer a solution-based mechanism dominated by the formation of O<sub>2</sub><sup>−</sup>. When O<sub>2</sub> is reduced to O<sub>2</sub><sup>−</sup>, larger cations stabilise O<sub>2</sub><sup>−</sup> through ion-pair formation (ionic bonding), which allows a less negative  $E_{1/2}$  for CsO<sub>2</sub> formation than for NaO<sub>2</sub>.<sup>11,69</sup> The polarisability of the ionic bond decreases (the bond becomes more covalent in nature) for smaller alkali metals,<sup>26</sup> and therefore, such entities present increased peak separation in the voltammetric response and a more negative  $E_{1/2}$ . The fact that surface-adsorbed NaO<sub>2</sub> formed at the surface may also block metal active sites, thus inhibiting further ORR, may also play a part in the increase in ORR overpotential observed for Na<sup>+</sup> relative to Cs<sup>+</sup> in Fig. 4.

Differences in the peak current intensities among alkali metals are also observed in Fig. 4. The ratio of current between the O<sub>2</sub><sup>−</sup> (I) and the O<sub>2</sub><sup>2−</sup> (II) peaks is close to 1 for Na<sup>+</sup> and decreases for larger cations in the order Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup>.



This asymmetry could be related to the lifetime of the formed  $O_2^-$  complex.  $O_2^-$  in the presence of large cations could readily be solvated back into solution, which would reduce the number of species on the surface to undergo the second reduction to  $O_2^{2-}$  (II), which in turn results in lower currents and a more negative potential for the onset of the second reduction to  $O_2^{2-}$ . In addition, the separation of peaks I and II may also be affected. Upon the formation of strongly adsorbed  $NaO_2$  at the surface of Pt(111), quantitative and rapid activation towards the formation of  $Na_2O_2$  *via* Pt surface catalysis might be taking place. This would result in two effects in agreement with the data presented: (i) the intensity ratio of peak I to peak II being close to unity and (ii) the difference in potential between peaks I and II reflecting the extent of surface interaction of the adsorbed  $MO_2$  complex (smallest peak separation for  $Na^+$ ). Additionally, the intensity of the peak related to the oxidation of  $O_2^{2-}$  (III) also decays for larger cations ( $Na^+ > K^+ > Cs^+$ ). In this sense, larger cations complexing with  $O_2^{2-}$  seem to have a more labile/dissociating nature compared to smaller cations, which would explain the lower intensity for the  $Cs_2O_2$  electrooxidation (III) (upon formation, the complex decays or diffuses away prior to the positive-going sweep, leading to a lower intensity).

In order to further study the surface-dependence of the ORR among different alkali cations without the possibility of  $O_2$  diffusion influencing the results, cyclic voltammetry in  $O_2$ -saturated DMSO containing  $Na^+$ ,  $K^+$ , and  $Cs^+$  was recorded,

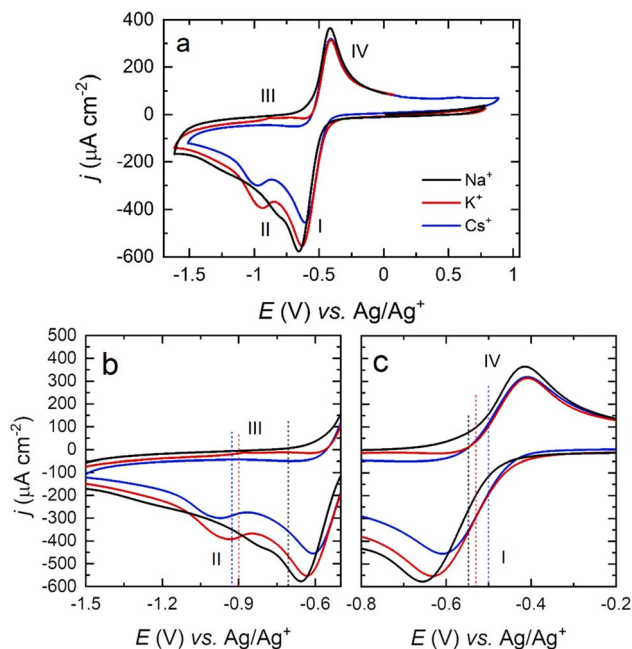


Fig. 5 (a) Cyclic voltammograms of a Pt(poly) electrode in an  $O_2$ -saturated DMSO solution containing 0.1 M  $NaClO_4$  (black),  $KClO_4$  (red) and  $CsClO_4$  (blue), at  $50\text{ mV s}^{-1}$  scan rate. Expanded view of the potential range corresponding to the formation of  $O_2^{2-}$  (b) and  $O_2^-$  (c). Dotted lines represent the  $E_{1/2}$  of the ORR half reactions for  $Na^+$  (black),  $K^+$  (red) and  $Cs^+$  (blue).





using a Pt polycrystalline disk electrode immersed in the electrolyte (no meniscus, Fig. 5).

The trends in the position of  $E_{1/2}$  for the first and second reduction of  $O_2$  as a function of metal cation are comparable both for Pt(111) and Pt(poly) electrodes (Table 2), with a small variation of *ca.* 30–40 mV associated with differences in surface structure.

While the current density ratio between the  $O_2^-$  (I) and  $O_2^{2-}$  (II) peaks is equivalent between Pt(111) and Pt(poly) using larger cations, *i.e.*,  $K^+$  and  $Cs^+$ , the ratio in  $Na^+$ -containing DMSO differs, with a ratio close to 1 for Pt(111) and a ratio  $>1$  for Pt(poly). Other previous studies have highlighted that both the surface and electrolyte have an impact on the  $Na^+$ -ORR mechanism.<sup>30</sup> In DMSO, Pt(110) and (111) facets support the formation of  $Na_2O_2$  as the main reduction product on the surface, while on Pt(100) and polycrystalline surfaces, the formation of  $NaO_2$  is less favoured and desorption and solvation is reported,<sup>4,13</sup> attributed to a more limited surface interaction of oxygen with electrode surfaces that do not contain {111} and {110} terrace sites.<sup>24</sup> This finding is consistent with the lower intensity of the redox peak associated with the formation of  $Na_2O_2$  on Pt(poly) surfaces compared with Pt(111) and Pt(110). The  $NaO_2$  surface complex in this case is less strongly interacting with the surface, so the activation of the second reduction step by the Pt(100) surface is much less marked, resulting in a lower intensity for peak II.

The difference in the relative current densities of the  $M^+-O_2^{2-}$  complex on the forward and reverse sweeps shows the same trend as for Pt(111) ( $Cs^+ > K^+ > Na^+$ ), consistent with the dissociation/lability of the  $O_2^{2-}$  complex for larger cations, which suggests that  $Cs^+$ -ORR chemistry would be mostly dominated by solution-phase processes rather than being surface controlled.

While careful control of the crystal facet influences the reaction pathway, this is highly dependent on the cation of choice, as can be observed in Fig. 6. Shifts in the peak potential between the (111) and (100) facets for  $Na^+-O_2$  OER/ORR are significant, whilst being negligible for  $Cs^+$ , differing by as much as  $\pm 0.2$  V for the first reduction and  $\pm 0.3$  V for the second reduction when  $Na^+$  cations are present. These results again suggest that the surface structure has less effect on the ORR for larger alkali metals. The relative strength of adsorption for the peroxy- and superoxy-ion pairs would govern this behaviour, with those moieties formed by  $Cs^+$  cations giving rise to the weakest surface interactions. This assertion is borne out during spectroscopic measurements, to be outlined below.

The change in nature for the ionic bond<sup>26</sup> between alkali cations and the  $O_2^-$  directly depends on the cation size, and increased polarisability of the ionic bond for larger alkali metals may affect the stability of superoxide complexes. To investigate the stability of  $O_2^-$  as a function of potential in the presence of a larger cation, *in situ* SHINERS spectra were collected with a Pt(111) electrode in 0.1 M  $CsClO_4/DMSO$  (Fig. 7a). The intensity of the band centred at  $1160\text{ cm}^{-1}$ , corresponding to  $\nu_{(O-O)}$  in  $O_2^-$ , can only be observed at  $-0.55$  V, which correlates with the onset potential for the first reduction of  $O_2$  to  $O_2^-$ . The band fades at more negative potentials, associated with the desorption of  $O_2^-$  from the surface of the electrode. These results differ from those previously reported for  $Na^+$  in DMSO, where the band associated with  $\nu_{(O-O)}$  can be observed even up to  $-1.0$  V (at  $1154\text{ cm}^{-1}$ ).<sup>24</sup>



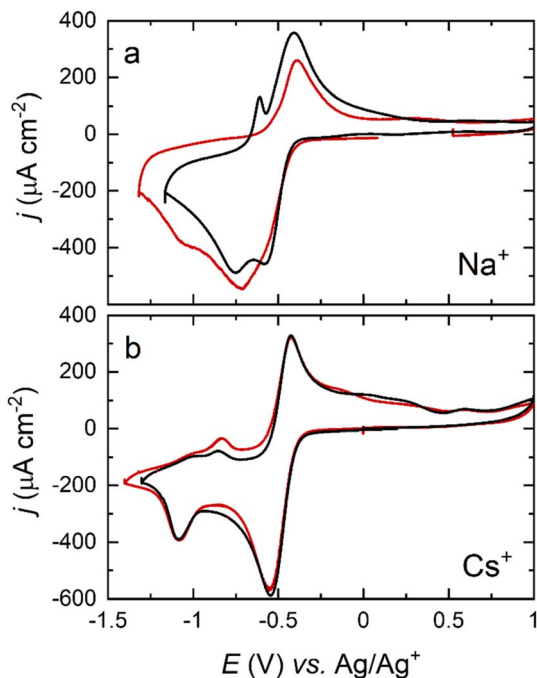


Fig. 6 Cyclic voltammograms of a Pt(111) (black) and a Pt(100) (red) electrode in an  $\text{O}_2$ -saturated DMSO solution containing (a) 0.1 M  $\text{NaClO}_4$  and (b) 0.1 M  $\text{CsClO}_4$ . Scan rate:  $50 \text{ mV s}^{-1}$ .

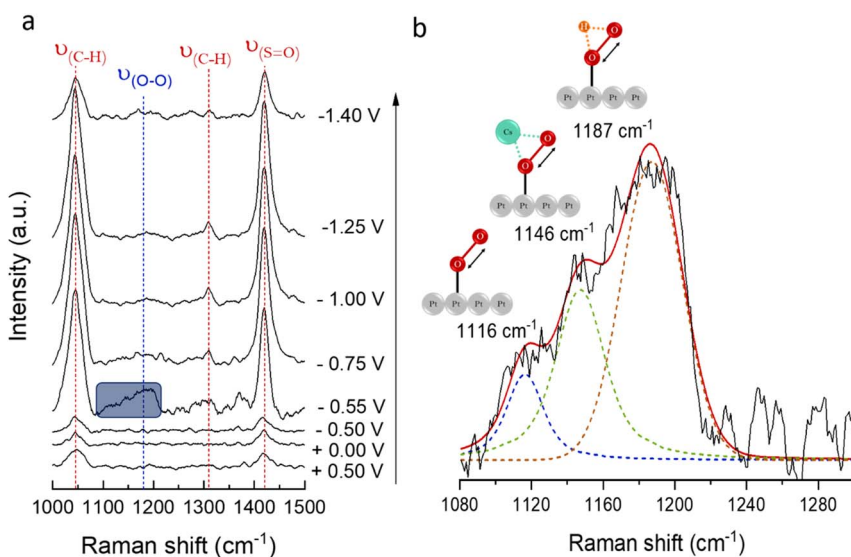


Fig. 7 (a) Potential-dependent *in situ* SHINERS spectra obtained from a Pt(111) electrode in a solution containing 0.1 M  $\text{CsClO}_4/\text{DMSO}$ , purged with Ar and, subsequently, saturated with  $\text{O}_2$ . (b) Voigt model fitting of  $\nu_{(\text{O}-\text{O})}$  at  $-0.55 \text{ V}$ .



The deconvolution of the band centred at  $1160\text{ cm}^{-1}$  is shown in Fig. 7b. The broad  $\nu_{(\text{O}-\text{O})}$  band has contributions from free  $\text{O}_2^-$  at  $1116\text{ cm}^{-1}$ ,  $\text{CsO}_2$  at  $1146\text{ cm}^{-1}$ , and  $\text{HO}_2$  (most likely from minor traces of  $\text{H}_2\text{O}$  in the electrolyte) at  $1187\text{ cm}^{-1}$ .<sup>26,70</sup>

The  $\nu_{(\text{O}-\text{O})}$  frequency shifts depend on the strength of the bond between the alkali cation and the  $\text{O}_2^-$ . Hence, the higher frequency observed for  $\nu_{(\text{O}-\text{O})}$  ( $\text{NaO}_2$ ) at  $1161\text{ cm}^{-1}$ ,<sup>71,72</sup> compared to  $\nu_{(\text{O}-\text{O})}$  ( $\text{CsO}_2$ ) at  $1146\text{ cm}^{-1}$ ,<sup>13,24,26,73</sup> may be ascribed to the ionic radii of the cations, *i.e.*, smaller cations display a substantial electrostatic force that strongly attracts the valence electrons from  $\text{O}_2^-$  and, therefore, present a stronger bonding interaction with the  $\text{O}_2^-$ . Additionally, while no free  $\text{O}_2^-$  has been detected in the presence of  $\text{Na}^+$  (at equal alkali-metal concentrations),<sup>24</sup> spectroscopic evidence of the presence of free  $\text{O}_2^-$  ( $1116\text{ cm}^{-1}$ ) in  $\text{Cs}^+$ -containing electrolytes (Fig. 7b) demonstrates the dissociation of  $\text{O}_2^-$  back into solution in the presence of larger cations.

Bands at  $1040$  and  $1310\text{ cm}^{-1}$  correspond to the methyl-group rocking modes in DMSO and that at  $1420\text{ cm}^{-1}$  to  $\nu(\text{S}=\text{O})$ .<sup>74-76</sup> The bands associated with DMSO vibrations increase at  $-0.55\text{ V}$ , coinciding with the formation of  $\text{O}_2^-$  species at the electrode|electrolyte interface. Enhanced band intensity for DMSO at this potential may be due to the solvation of  $\text{O}_2^-$ , *i.e.*,  $\text{Cs}^+(\text{DMSO})_4(\text{O}_2^-)$ . The further uptake of DMSO onto the Pt(111) surface following desorption of  $\text{Cs}^+(\text{DMSO})_4(\text{O}_2^-)$  species is also indicated by the significant increase in DMSO bands after this point. Increased DMSO band intensity in the potential range where ORR occurs has not been observed for  $\text{Na}^+$ ,<sup>24</sup> probably due to DMSO less successfully competing for Pt sites with more strongly adsorbed  $\text{NaO}_2$ , *i.e.*, smaller cation- $\text{O}_2^-$  complexes are more strongly adsorbed on the Pt(111) surface, while for larger cation- $\text{O}_2^-$  complexes, adsorption is weaker, and they are readily desorbed back into solution. The lower intensity of the DMSO bands at  $-1.4\text{ V}$  could result from a potential-dependent reorientation of DMSO on the surface, similar to that reported for the reorientation of acetonitrile on roughened Au surfaces.<sup>77</sup>

## Conclusions

The ORR and OER have been studied on Pt(111) and Pt(100) single crystals and on a polycrystalline Pt disk, using a non-aqueous solvent, dimethyl sulfoxide (DMSO), in the presence of alkali-metal perchlorate salts. Voltammetric results show that the cation size strongly affects the mechanism of the ORR in  $\text{O}_2$ -saturated DMSO-based electrolyte.

In contrast to  $\text{Na}^+$ , surface structure has been proved not to significantly influence the reaction pathway involving  $\text{Cs}^+$  cations. This behaviour is ascribed to the relative surface adsorption strengths of superoxy and peroxy ion-pair complexes formed when utilising different cations. We conclude that because no changes were detected in the voltammetric profile of the ORR in the presence of  $\text{Cs}^+$  cations using polycrystalline Pt, Pt(111) and Pt(100) electrodes, this supports a preferred solution-based mechanism with a lower impact of the surface structure compared to smaller cations, such as  $\text{Na}^+$ . Shifts in the  $E_{1/2}$  and changes in the intensities of redox peaks I to IV as a function of cation size are also consistent with this finding. Moreover, the separation in potential between peaks I and II is suggested to be a marker for the extent of interaction between the electrode surface and  $\text{MO}_2$ . Because of this, it is speculated that activation of this



surface complex to facilitate the second electron transfer to form peroxy species will be promoted as cation size decrease, *i.e.*, the ORR pathway preference changes as the cation size increases, from  $\text{O}_2^{2-}$  formation in the case of  $\text{Na}^+$  (and indeed  $\text{Li}^+$ ) to  $\text{O}_2^-$  formation for larger cations, *i.e.*,  $\text{K}^+$  and  $\text{Cs}^+$ .

To assess this proposal, the stability of the  $\text{O}_2^-$  complex adsorbed at the surface was studied with *in situ* Raman spectroscopy in  $\text{Cs}^+$ -containing electrolytes and results demonstrated the formation of  $\text{CsO}_2$  in a limited potential range, commensurate with the first reduction peak, but this species readily desorbs into solution. The labile nature of the surface  $\text{O}_2^-$  bond is consistent with the lack of structural sensitivity in CV, suggesting a solution-based ORR/OER mechanism for larger cations. This may disfavour subsequent reduction to  $\text{O}_2^{2-}$  when using  $\text{Cs}^+$  compared to  $\text{Na}^+$  and this is made manifest by the relative magnitudes of peroxy- and superoxy-redox peaks highlighted above. Furthermore, *in situ* Raman spectroscopy indicates that the displacement of  $\text{CsO}_2$  species may be ascribed to uptake of DMSO at the interface, interacting strongly with the surface and causing displacement of ion pairs at potentials where the ORR occurs. This study highlights the possibility of using large alkali-metal cations, such as  $\text{Cs}^+$ , in the electrolyte of Li and Na– $\text{O}_2$  cells to tailor the initial ORR pathway towards a one-electron transfer and thus, contributing to preventing the formation of surface-blocking peroxide intermediates.

## Author contributions

All authors have contributed to writing, reviewing, and editing the final version of the manuscript. JFV contributed with investigation, methodology, data curation, conceptualisation, formal analysis, visualisation, and writing of the original draft. LJH contributed with funding acquisition, conceptualisation, formal analysis, supervision, resources, and project administration. GC contributed to investigation and methodology. GAA contributed to visualisation, supervision, formal analysis, and conceptualisation.

## Conflicts of interest

All authors declare no conflict of interest.

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