

## Supporting Information

# How the Nature of the Alkali Metal Cations Influences the Double Layer Capacitance of Cu, Au and Pt Single Crystal Electrodes

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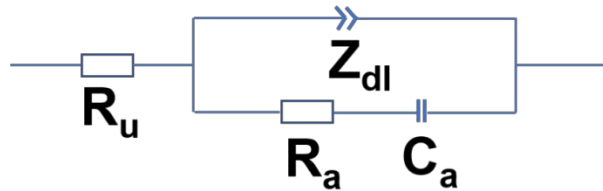
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## S1. The used equivalent electric circuit

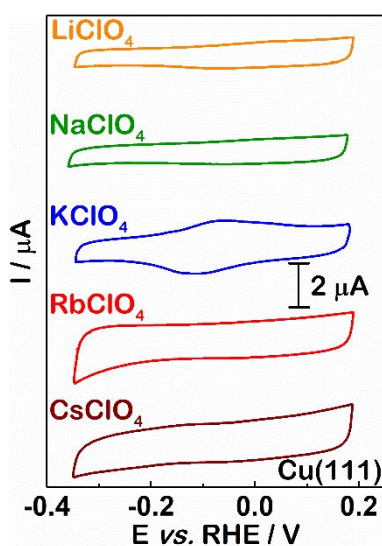
**Figure S1** shows the equivalent electric circuit used in this work. A constant phase element (CPE) ( $Z_{dl}$ ) and resistance ( $R_u$ ) were used to describe the double layer capacitance and the uncompensated resistance of the electrolyte, respectively. The additional adsorption resistance ( $R_a$ ) and adsorption capacitance ( $C_a$ ), connected in series, account for possible adsorption of  $\text{OH}^*$  and  $\text{H}^*$  species close to the potential of zero charge.<sup>1</sup> In the studied cases at the regions near to the potential of zero charge the  $R_a$  values becomes large and the  $C_a$  ones become small; therefore, the overall contribution comes mainly from the double layer capacitance.



**Figure S1.** Equivalent electric circuit used for the fitting of the obtained impedance results in all the measurements.  $R_u$  represents the uncompensated resistance of the electrolyte;  $Z_{dl}$  is the double layer impedance;  $R_a$  is the adsorption resistance; and  $C_a$  is the adsorption capacitance.

## S2. CVs of Cu(111) in 0.1 M $MeClO_4$

**Figure S2** shows typical CVs of Cu(111) in the investigated electrolytes. Small peaks observed in  $KClO_4$  are presumably from weak adsorption of  $ClO_4^-$ .



**Figure S2.** Cyclic voltammograms for Cu(111) electrodes in Ar saturated 0.05 M  $MeClO_4$  ( $Me^+$  =  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ). Potential scan rate is 50 mV/s.

### S3. CVs of Cu(100) in 0.1 M $MeClO_4$

Figure S3 shows typical CVs of Cu(100) in the investigated electrolytes.

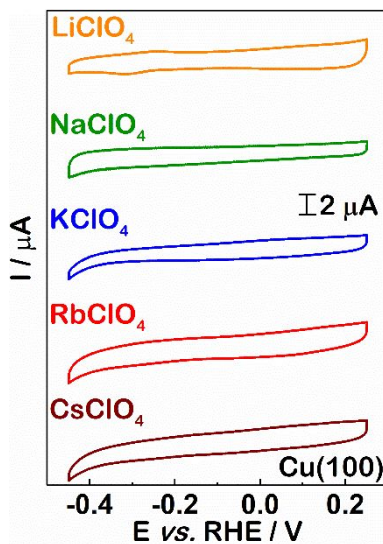
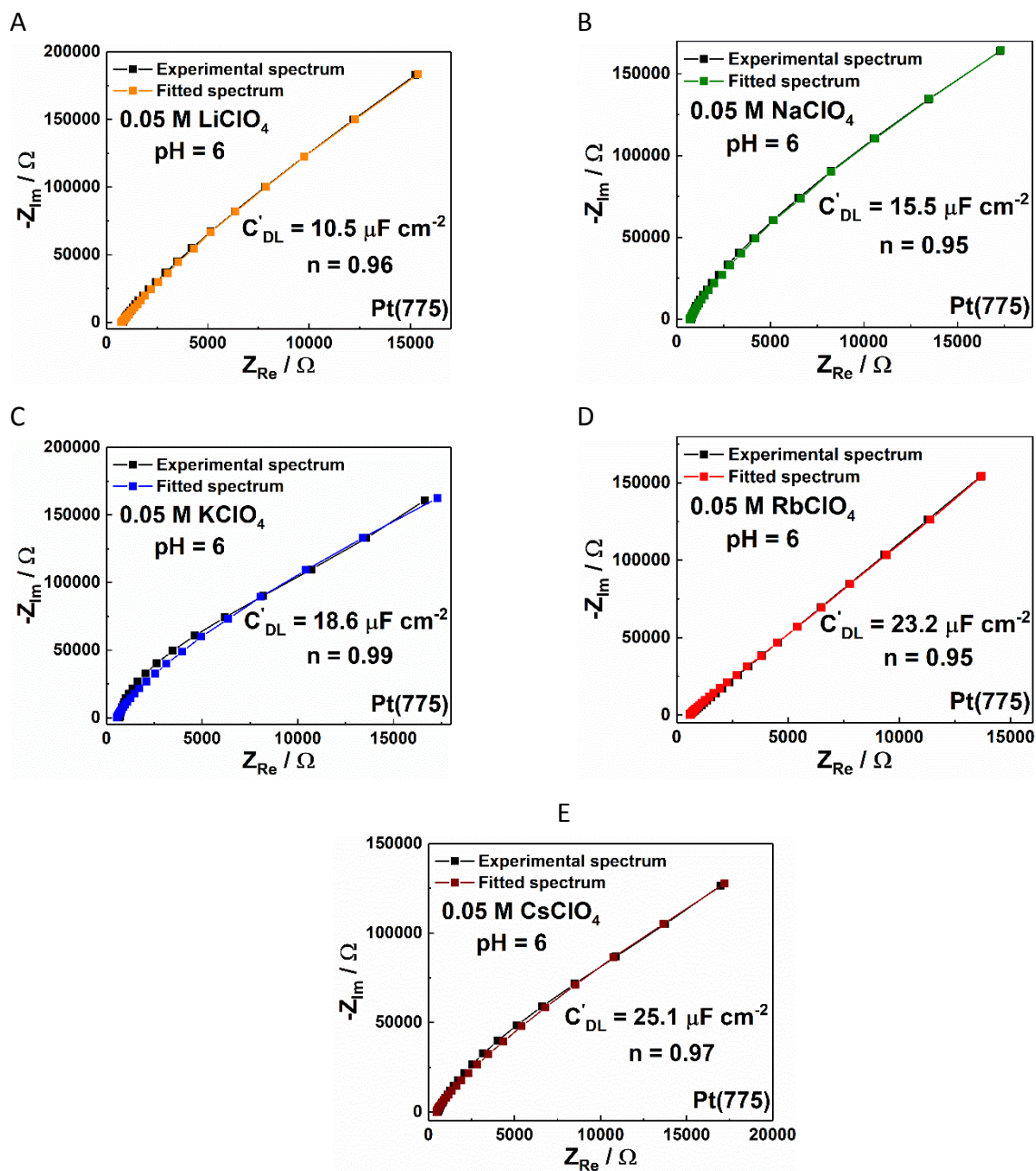


Figure S3. Cyclic voltammograms characterizing Cu(100) electrodes in Ar saturated 0.05 M  $MeClO_4$  ( $Me^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$ ) electrolytes. The potential scan rate is 50 mV/s.

### S4. The fitted and experimental EIS data for Pt(775)

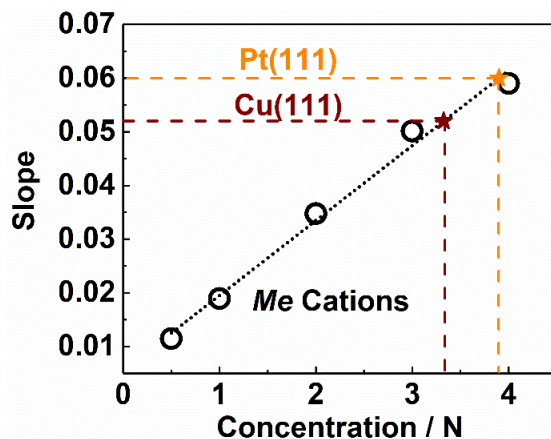
Figure S4 gives typical examples of fitted and experimental impedance spectra. The fitted EIS curves were in accordance with the experimental curves. Moreover, the parameter  $n$  in the CPE was close to one ( $n > 0.95$ ) when there was no Faradaic reactions. Therefore, one can assume that the experimentally measured,  $C'_{DL}$ , is equal to the actual double layer capacitance,  $C_{DL} \approx C'_{DL}$ .



**Figure S4.** Examples of the fitted and experimental spectra of Pt(775) in 0.05 M (A) LiClO<sub>4</sub>, (B) NaClO<sub>4</sub>, (C) KClO<sub>4</sub>, (D) RbClO<sub>4</sub>, and (E) CsClO<sub>4</sub> at pH 6. The obtained parameters of CPE, namely, the double layer capacitance,  $C'_{DL}$ , and the factor,  $n$ , are also shown.

### S5. Slopes as the functions of the concentrations of alkali metal cations

The slopes obtained for the Pt(111) and Cu(111) electrodes, 0.060 and 0.052 (taken from Figure 4 and Figure 2A), correspond to the effective concentrations of alkali metal cations being  $\sim 4.0$  and  $\sim 3.4$  M, respectively. The bulk concentration of alkali metal cations is 0.05 M. Therefore, for both copper ( $\sim 3.4$  M/0.05 M  $\approx 68$ ) and platinum ( $\sim 4.0$  M/0.05 M  $\approx 80$ ) electrodes, the near-surface concentration of alkali metal cations is more than 60 times higher than the bulk concentration.



**Figure S5.** Slopes adapted from Figure 2B and Figure 4 as the functions of the concentrations of alkali metal cations (*Me* cations). The slopes obtained for the Pt(111) and Cu(111) electrodes were also added ( shown by the star symbols).

## S6. CVs of Pt(775) and Pt(12 10 5) in 0.1 M HClO<sub>4</sub>

Figure S6 shows CVs of Pt(775) and Pt(12 10 5) measured in 0.1 M HClO<sub>4</sub> after the electrode preparation. The obtained CVs are comparable to those “finger-print” CVs from the literature.

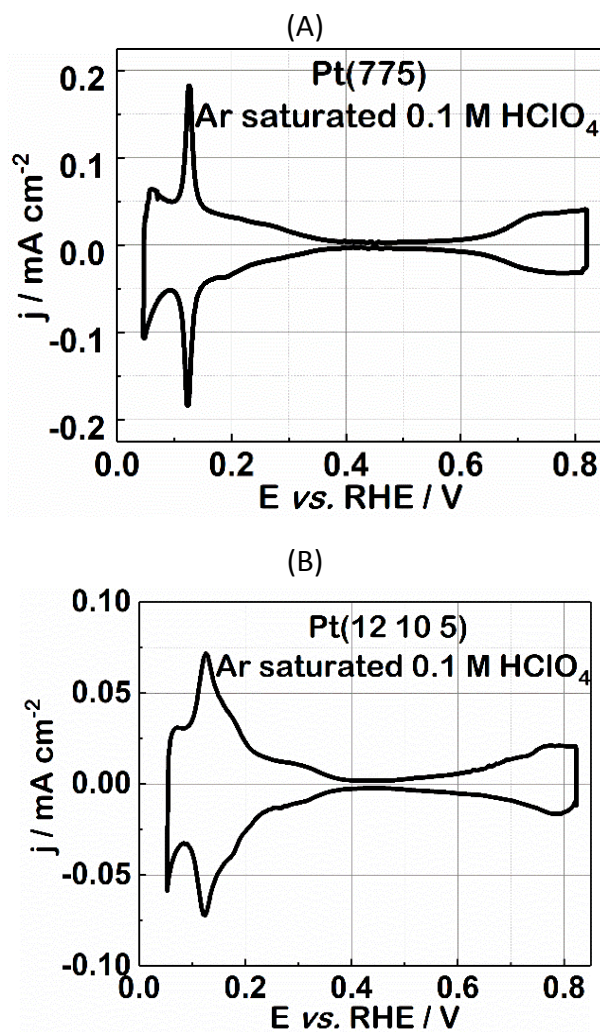
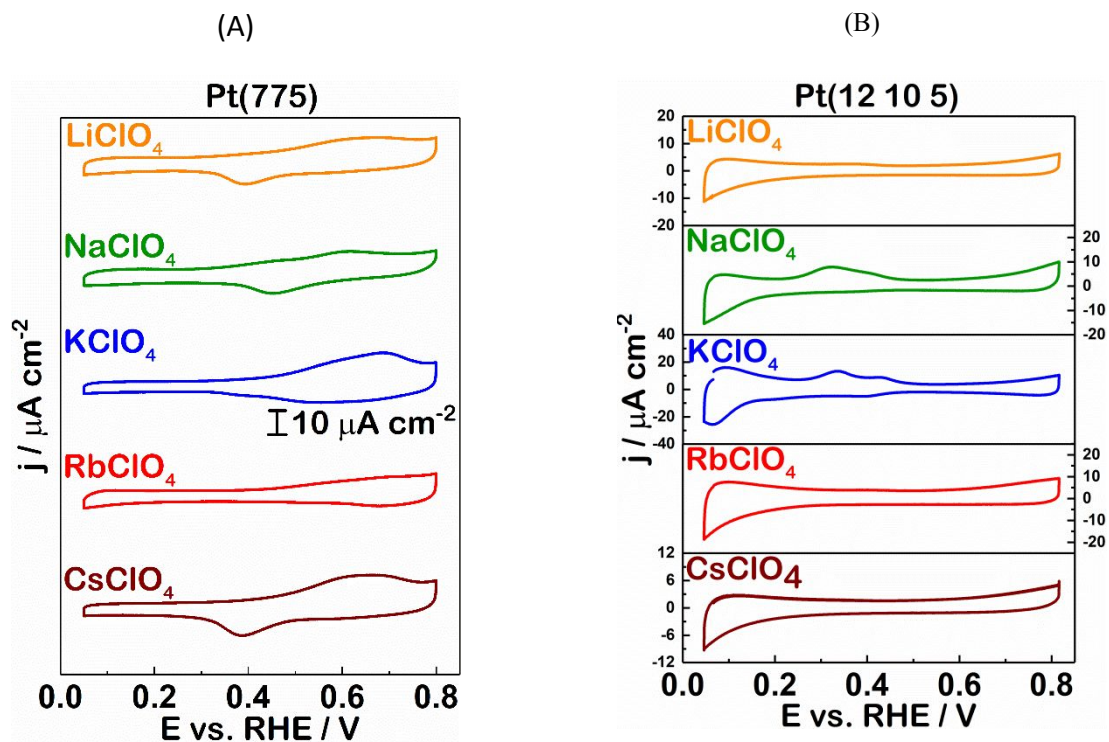


Figure S6. Characteristic cyclic voltammograms of (A) Pt(775), and (B) Pt(12 10 5) in Ar saturated 0.1 M HClO<sub>4</sub> using hanging meniscus configuration (scan rate: 50 mV/s).

S7. CVs of Pt(775) and Pt(12 10 5) in 0.1 M  $MeClO_4$



**Figure S7.** Examples of cyclic voltammograms for (A) Pt(775) and (B) Pt(12 10 5) electrodes in Ar saturated 0.05 M  $MeClO_4$  ( $Me^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$ ). The potential scan rate is 50 mV/s.



### S8. Double layer capacitances as a function of the electrode potential for Pt(111), Pt(775) and Pt(12 10 5) electrodes in 0.1 M HClO<sub>4</sub>

Figure S8 shows  $C'_{DL}$  of Pt(111), Pt(775) and Pt(12 10 5) at different electrode potentials in Ar saturated 0.1 M HClO<sub>4</sub>. No Faradaic reactions are observed at the potential where  $C'_{DL,MIN}$  is measured (see Figure S6). The EDL capacitance increases with increasing the number of terrace atoms, as follows: Pt(12 10 5) < Pt(775) < Pt(111).

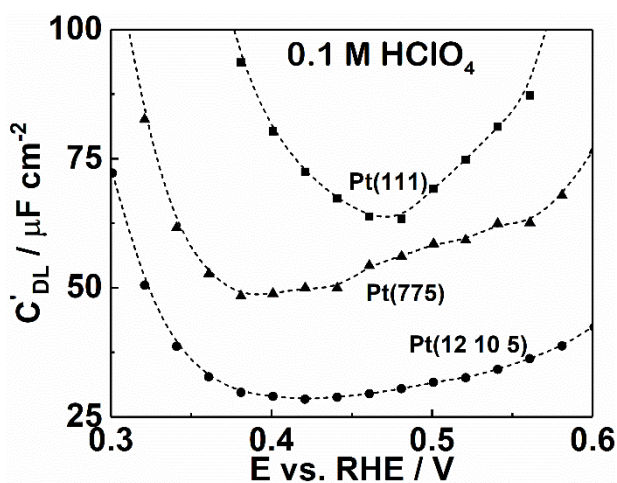


Figure S8. Examples of the double layer capacitances as a function of the electrode potential for Pt(111), Pt(775) and Pt(12 10 5) electrodes in Ar saturated 0.1 M HClO<sub>4</sub>. The dashed lines are added as guides to eyes.

### References

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- (1) Garlyyev, B.; Xue, S.; Watzele, S.; Scieszka, D.; Bandarenka, A. S. Influence of the nature of the alkali metal cations on the electrical double layer capacitance of model Pt (111) and Au (111) electrodes. *J. Phys. Chem. Lett.* **2018**, *9*, 1927-1930.