# A suitable electrolyte for high pressure $CO_2$ reduction? Investigation of conductivity and salt spectrum in "alcoholic potash".

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## 1. Introduction

The electrification of chemistry is an important step for achieving the climate goals. For this purpose, the electrochemical reduction of $CO_2$ is one of the most attractive reactions due to its high flexibility and product diversity.[1] Two major problems are currently emerging in the process, which influence each other. Either the current density is too low to obtain a technically relevant product yield per time or hydrogen evolution is favored instead of organic reaction products. The current density can be increased by the higher conductivity of saline electrolytes. In turn, the selectivity of organic products can be improved by the use of supercritical $CO_2$.[2] The combination of these two approaches is currently a challenge because classical aqueous electrolytes lead to the favoring of hydrogen evolution due to the low solubility of $CO_2$ in water. One approach is to use saline organic solvents as electrolytes, since the solubility of supercritical $CO_2$ in organic substances is significantly higher than in water.

Potassium hydroxide has the potential to increase conductivity and consequently current density because its $K^+$ and $OH^-$ ions have a high limiting molar conductivity.[3] In addition, short-chain alcohols exhibit both complete miscibility with $CO_2$ at high pressure[4] and good solubility of potassium hydroxide[5]. Therefore, the aim of this work is to investigate alcoholic potassium hydroxide solutions in terms of their conductivities at ambient pressure and in compressed $CO_2$ atmosphere, respectively. In addition, different potassium salt species are present at these conditions and will be analyzed in more detail.

## 2. Materials and Methods

First, the conductivities of methanol, ethanol and 2-propanol were studied as a function of potassium hydroxide concentration at ambient pressure and 25 °C. For these measurements the 4-pole conductivity sensor Tetra Con 325 together with the conductometer cond 3310 from WTW (Germany) were used. Subsequently, the conductivity of methanol containing potassium hydroxide was measured under a compressed $CO_2$ atmosphere up to 80 bar. Because of the temperature range of the reaction the measurement was performed at 40 °C as well as 80 °C. Therefor the 2-pole conductivity sensor type EL 23 together with the conductometer FLB 1 from IGEMA GmbH (Germany) were used. It should be noted that the potassium hydroxide reacts with both methanol and $CO_2$. XRD was used to identify the salt species in the system. To do this, the solvent of the electrolyte was removed until dry salt remained, after the conductivity measurement. The salt was then ground and analyzed. The materials used are described in Table 1.

**Table 1.** Material description.

| Material | CAS | Source | Purity | Purification method |
|---|---|---|---|---|
| Methanol | 67-56-1 | VWR<br>(AnalaR NORMAPUR®) | 99.80 % | None |
| Ethanol | 64-17-5 | Fisher scientific | 99.80 % | None |
| 2-Propanol | 67-63-0 | Carl Roth (ROTIPURAN®) | 99.80 % | None |
| Potassium hydroxide | 1310-58-3 | Carl Roth (ROTI®METIC) | 99.98 % | Vacuum drying<br>120 °C; 0.1 bar; 24 h |
| Carbon dioxide | 124-38-9 | Air liquide | 99.995 % | None |

## 3. Results and discussion

The results of conductivity measurements of various alcohols as a function of potassium hydroxide concentration at ambient pressure can be found in Figure 1. One of the most important results is the increase of the conductivity with decreasing chain length of the alcohols. This can not only be explained by the decreasing solubility of the salts, since different conductivities are observed even at the same salt concentration. The main reason is the decreasing OH-acidity with increasing chain length of the alcohols. Furthermore, all plots show a maximum. Thus, an increase of the concentration is not always effective if the highest possible conductivity is to be achieved.

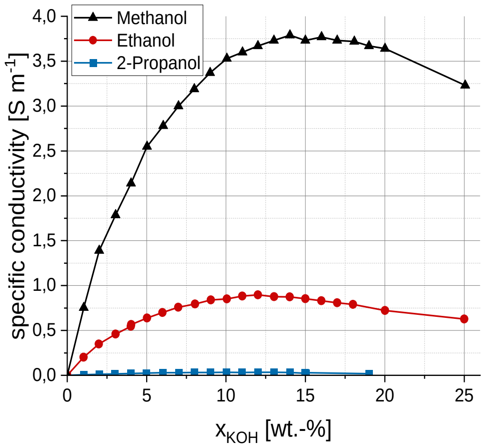


**Figure 1.** Specific conductivity as a function of KOH concentration at ambient pressure and 25 °C.

Based on the measurements at ambient pressure, only methanol containing potassium hydroxide with a conductivity up to 3.79 S/m seems to be a suitable electrolyte. Thus, the measurements at high pressure are performed with methanol only. Figure 2 shows the influence of compressed $CO_2$ on the conductivity of a methanol-potassium hydroxide solution. It can be seen that the conductivity increases with increasing temperature. Initially, the conductivity decreases with increasing pressure. Above 60 bar, the conductivity at 40 °C seems to be approximately constant. At 80 °C the conductivity decreases linearly with increasing pressure. It should be noted that no linearity can be observed at 5 % and 80 °C, since the measured conductivity at 30 bar is outside the measuring range of the sensor.

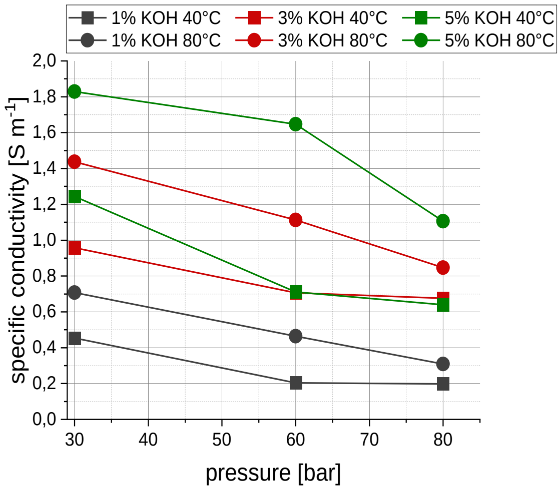


**Figure 2.** Specific conductivity as function of $CO_2$ pressure with different KOH concentrations and at 40°C & 80 °C.

## 4. Conclusion

To the first series of measurements at ambient pressure, only methanol containing potassium hydroxide seemed to be a promising electrolyte for electrochemical $CO_2$ reduction. However, during the measurement in the high-pressure range, it turned out that the supercritical $CO_2$ reduces the conductivity of the electrolyte by up to 80 %. This is primarily due to the reaction between $CO_2$ and KOH because the reaction products have a lower conductivity in methanol. In addition, a precipitation was observed, which reduces the salt concentration in the solvent.

Accordingly, KOH, which is often used for electrolytes, is not favorable for the reduction of supercritical $CO_2$.

### References

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